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Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers under Project 4A162720D048, "Industrial Operations Pollution Control Technology"; Work Unit EP-UC5, "Studies of Pyrolytic Behavior of Energetic Materials." The technical monitor was Richard Eichholtz, SFIM-AEC-TS.

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL principal investigator was Dr. Donald M. Cropek. Interpoll Laboratories, Inc., is acknowledged for performing the sample collection. Appreciation is extended to the Illinois Waste Management and Research Center for analysis of several collected samples. Arthur D. Little is recognized for technical assistance, and Radford Army Ammunition Plant is recognized for incinerator operation and their cooperation is greatly appreciated. This research was supported in part by an appointment to the Research Participation Program at CERL administered by the Oak Ridge Institute for Science and Education through an interagency agreement between U.S. Department of Education and CERL. The technical editor was Linda L. Wheatley, Information Technology Laboratory. Dr. Ilker Adiguzel is Chief, CN-E, Dr. John T. Bandy is Chief, CN; and Gary W. Schanche is the associated Technical Director, CVT. The Acting Director of CERL is Dr. Alan W. Moore.

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1 Introduction

Background

Demilitarization activities and hazardous waste disposal practices by the military are increasingly scrutinized by environmentalists and the public. Care must be taken to lessen public concerns and minimize perceived and real risks. The military is using open burning/open detonation (OB/OD) as the primary demilitarization method for its off-specification energetic material (EM) and energetic wastes (EW) from both propellants and explosives. OB/OD is uncontrolled thermal decomposition performed outdoors in a pit or on a slab (AEC 1999). All resultant combustion products are released into the environment. The effect on the environment from the repetitive direct release of by-products and the accompanying noise is uncertain. The environmental concern surrounding OB/OD has led the military to examine several alternative technologies to dispose of over 400,000 tons of accumulated conventional munitions and propellants, explosives, and pyrotechnics (Black 1997).

EMs are organic compounds of high potential reactivity or ignitability, which makes them ideally suited for incineration — controlled combustion at high temperature in the presence of excess oxygen. In contrast to OB/OD, the thermal process is carried out in an enclosed chamber with extensive emission control equipment. The U.S. Environmental Protection Agency (EPA) strictly regulates the operation of an incinerator under the Resource Conservation and Recovery Act (RCRA) through a permit containing explicit performance standards (Garrett 1994). The EPA uses trial burns to establish the performance standards and other requirements in order to protect the public and environment from toxic emissions. These emissions include principal organic hazardous constituents (POHC), which are compounds initially present in the waste, or products of incomplete combustion (PIC), which are organic by-products resulting from the incomplete degradation of POHC (Dellinger et al. 1986).

Incineration is frequently used for hazardous waste treatment and disposal (Avogadro and Ragaini 1994). Incineration is a mature technology recognized by the EPA as a Best Demonstrated Available Technology. The rotary kiln incinerator is a common design that allows for simple application to a wide range of organic compounds in many forms (Ayers 1994). Several military facilities have

incorporated incineration in the management of hazardous waste. The Army incinerates various EW at five different sites and has plans for several additional EW incinerators in the near future (Subsinsky 1993).

Objective

This report describes the collection and characterization of incinerator emissions that evolve during the burning of three types of EM and EW.

Approach

An Army hazardous waste incinerator was used for burning EW. Three different wastes containing nitrate esters were selected for investigation. Sample collection was performed by an outside contractor, and sample analysis was done at both a state analytical laboratory and the Environmental Chemistry Laboratory at CERL.

Several different EPA collection techniques were used to collect as complete a subset of by-products as possible. Continuous emission monitors were used to measure light permanent gases such as oxygen (O_2), nitrogen oxides (NO_x), carbon monoxide (CO), and total hydrocarbons (THC). One collection train was used for hydrogen cyanide (HCN) analysis. Two collection methods were used for volatile and semivolatile organic species.

The results from the analysis of these collected samples give an emission profile for the incineration of a particular EW feed. The data from the incineration of nitroglycerin (NG) slums, nitrocellulose (NC) fines, and the double-base propellant AA2 will be presented in this report. Future research will compare the emission data generated here with data on bench scale pyrolysis of the same types of wastes. This comparison will help evaluate the usefulness of bench scale pyrolysis in modeling the incineration process.

Scope

This report will present the emissions characterization data from the incineration of AA2, NG, and NC wastes. Only nitrate ester containing waste feeds were available at this particular Army installation during the testing period.

It must be stressed that the data presented herein result from the analysis of samples collected just after the rotary kiln. These gases were intercepted before any further emission treatment or pollution control devices had an effect. The data shown here are not indicative or representative of the gases emitted from the stack but instead provide identification of the compounds produced by the initial thermal treatment.

Mode of Technology Transfer

It is anticipated that the information derived from this study will be incorporated into guidance for environmental representatives at military installations to help with decisions regarding demilitarization of EM, pollution control, and environmental clean up. In addition, the techniques and results will be of interest to incineration facilities to assist in selection of operation parameters, characterization of emissions, and evaluation of thermal treatment methods.

This report will be made accessible through the World Wide Web (WWW) at URL: http://www.cecer.army.mil.

2 Experimental Incinerator Design and Operation

The incinerator complex has been in operation since 1979. Its air pollution control systems were upgraded in 1993 to assure compliance with particulate and lead emission standards. The complex has two identical hazardous waste rotary kiln incinerator systems consisting of a rotary kiln, an afterburner, an evaporative cooler, and a baghouse. A schematic of the incinerator system is shown in Figure 1.
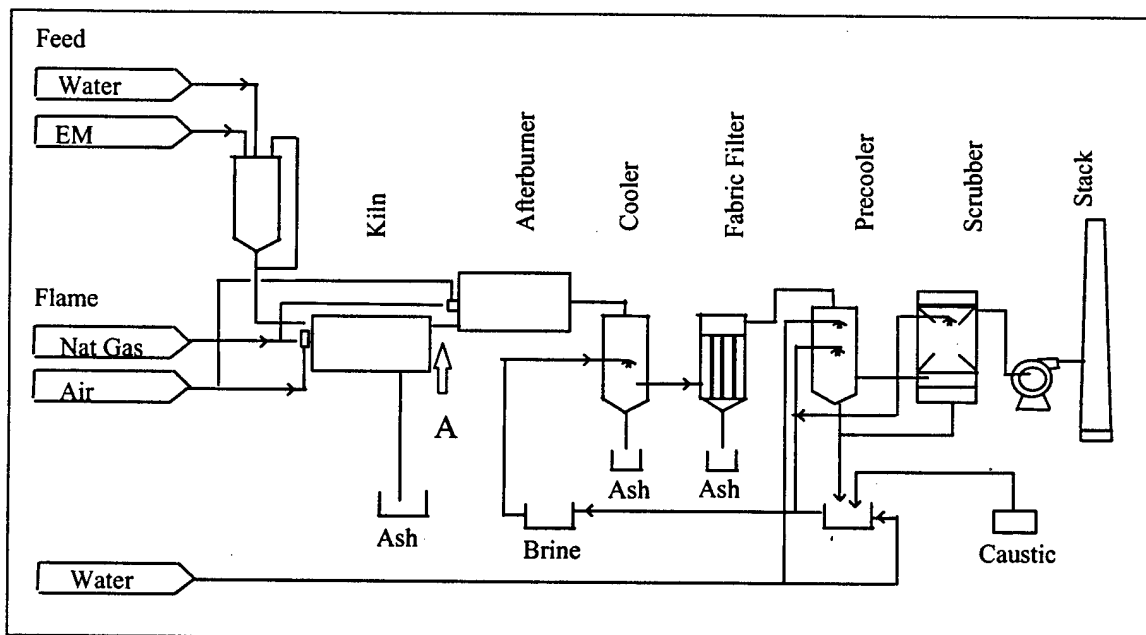
Figure 1. Schematic of a typical rotary kiln incinerator. Point A indicates the sampling point for the collection of by-products.

The rotary kiln is 12-ft long, 5.5 ft in diameter, and rotates at approximately 0.5 revolutions/minute. Waste streams are metered into the kiln at feed rates typically between 30 – 100 pounds of slurry per hour. During incineration, the kiln is maintained at temperatures near 1000 °F. Combustion occurs in the middle to rear sections of the kiln due to the waste stream evaporating and mixing with natural gas (fuel) and air (oxidant) as it passes through the 700 °F kiln inlet. The combustion products are kept in a gas phase as they continue to the kiln outlet at an elevated temperature of approximately 1370 °F. The gases then pass through a 1600 °F afterburner (secondary combustion chamber) to maximize deg-

radation. Exiting the afterburner, the gas stream is routed through an evaporative cooler and into a baghouse for particulate control.

The baghouse consists of 156 Goretex lined fiberglass bags, each 10-ft long and 6 in. in diameter. The accumulated residue or ash is collected in 55-gal drums for offsite disposal as a hazardous waste. The gases proceed through a wet scrubbing system for final polishing. To ensure compliance with permit conditions, stack CO concentrations are monitored. The waste feed automatically stops when the CO concentration exceeds 100 ppm with a 60-min rolling average.

Energetic Waste Samples

The EW available onsite during the incinerator testing period were NC fines, NG slums, and the double-base propellant AA2. The EW is mixed with water to create a low percent solid slurry feed (approximately seven parts water to one part solid waste). The NC fines waste feed is the simplest in chemical composition. A surfactant, NALCO 71-D5 antifoam, is added to the NC waste to prevent foaming of the slurry waste stream as it is fed into the incinerator. The NG slums comprise a trinary mixture of NG (90%), sawdust, and deactivator. The solventless propellant AA2 is predominantly composed of NC and NG (approximately 90%) together with additives including organometallic salts, triacetin, di-n-propyladipate, candelilla wax, and 2-nitrodiphenylamine (NDPA). Before incineration, the waste stream is subjected to a number of analyses as required by the incinerator permit, including screening for 14 metals and chlorine levels.

On day one, background level gases were established by operating the incinerator with no sample feed. On day two, samples were collected as 1080 lb of NC fines (75% water [H_2O]) were metered into the kiln at 83 lb/hr. On day three, samples were collected as 450 lb of NG slums were metered into the kiln at 37 lb/hr. On day four, samples were collected as 400 lb of AA2 were metered into the kiln at 39 lb/hr.

Sampling Methodology

Typical incineration sampling experiments collect by-products at the stack. Required ports and platforms are already present and conditions of the emission gases are frequently well known beforehand. The stack, however, is downstream of pollution control equipment that removes many species of interest to this research. Sampling in this study, therefore, was performed at the exit side of the kiln before the afterburner. This position is noted as point A on Figure 1. Sam-

ple collection at a point between the kiln and the afterburner resulted in a set of analytes truly representative of species produced during incineration and before further treatment.

Several problems were encountered when sampling at the exit side of the kiln: (1) the two ports available at this location would not allow simultaneous sampling of all gaseous by-products, (2) the high kiln temperature restricted the types of probes that could be used, (3) the 75-ft exclusion zone for personnel safety prevented close manipulation and observation of the samples during incineration of EM and EW, and (4) the orientation of the sampling ports relative to the gas stream did not allow isokinetic sampling.

The first problem was solved by judicious sample scheduling. While the CEM probe was continuously in place in port 1 and the semivolatile compound probe was continuously in place in port 2, there was sufficient space to include a second probe into port 1. The volatile compound probe and the HCN probe were thus exchanged as needed in port 1.

The second sampling problem was solved by using two water-cooled probes designed to operate at temperatures exceeding 1300 °F. Each probe was quartz lined to minimize adsorption and interference, while also having high temperature resistance.

The third problem was undesirable, but easily handled for minimal to no effect on sample collection. The 75-ft exclusion zone had the greatest potential impact on the CEM gas analysis and the semivolatile sample collection. While the semivolatile, volatile, and HCN samples were collected as near to the sampling port as possible, the CEM gas stream had to be transported outside the 75-ft exclusion zone to the measuring instrumentation. Concerns that compounds of interest would be adsorbed onto the line (and thus not detected) were circumvented by using a heated Teflon-lined sampling umbilical to transport the gaseous samples to the CEM analyzers. The semivolatile collection method usually dictates the standard practice of a manual probe traverse during sampling to ensure the collection of a representative sample. This particular sampling site, however, was a narrow outlet of the kiln, especially when compared to a typical large diameter stack and, therefore, a manual probe traversal was not deemed critical.

The orientation problem remained unsolved. The turbulent gas flows at the kiln outlet prevented usable velocity data; therefore, the semivolatile samples were collected anisokinetically based on rough calculations of the theoretical gas velocity. The collection of the semivolatile by-products anisokinetically was not likely

affected by any particulates present because the average kiln temperature was 1300 °F. This temperature is assumed to be high enough to keep the number of particulates low and to prevent condensation of the semivolatile species onto particulates. Thus, a representative sample of the semivolatile compounds was believed to have been obtained.

Four separate sampling trains were required for complete analysis of the kiln off-gases. One probe each was needed for volatile and semi-volatile species. A separate probe was used for HCN, and a final probe supplied a slipstream of off-gases to five continuous emission monitors (CEM) arranged in series for THC, NO_x, O_2, carbon dioxide (CO_2), and CO. The temperature of the kiln was continuously monitored with a thermocouple inserted in one of the ports.

Figure 2 is a schematic showing the port and probe positions between the kiln and the afterburner. Ports 1 and 2 are separated in space by approximately 1 ft. The volatile organic compounds (VOCs) are collected using a Volatile Organic Sampling Train (VOST) as fully described in EPA Method 0030 (EPA 1986a). This train is briefly shown in the schematic of Figure 2 at port 1.

The collection system uses two traps arranged in series. The front trap is Tenax GC (2,6-diphenylene oxide polymer; 35/60 mesh) and the second trap is Tenax GC and activated charcoal arranged in a back-to-back fashion. A complete VOC sample is the adsorbate fraction from the traps (individually or as a single set) plus the condensate fraction collected in the impinger water positioned between the traps. For good quality assurance/quality control (QA/QC), the front cartridge traps of the VOC collection pairs were spiked during the preparation stage with a 10 µl aliquot of bromofluorobenzene, toluene-d8, 1,2-dichloroethane-d4, and dibromofluoromethane, each at a concentration of 0.5 µg/ml in purge and trap grade methanol. These compounds are referred to as surrogate standards. Unfortunately, these four surrogate standards were never observed in any of the VOC samples, indicating that the spiking solution concentration was too low.

The semivolatile organic compounds (SVOCs) are collected using a Modified Method 5 (MM5) sampling train as fully described in EPA Method 0010 (EPA 1986b). This train is shown in the Figure 2 schematic at port 2. A single SVOC sample comprises a particulate filter fraction, an adsorbate fraction from the XAD resin trap, and a condensate fraction from impinger water. For good QA/QC, the XAD cartridges were spiked with 0.1 µl of p-terphenyl-d14 in GC grade methylene chloride at a concentration of 50 µg/ml. This compound is also referred to as a surrogate standard.

Although HCN is a VOC by EPA classification, samples of HCN were collected separately because of its acidic nature and water solubility. As shown in Figure 2, HCN was collected from port 1 using a filter and impinger water bubbler apparatus as described in National Institute for Occupational Safety and Health (NIOSH) Method 7904 for cyanide determination in gas and aerosol matrices (NIOSH 1994). A cellulose ester filter membrane of 37-mm diameter and 0.8-μm pore size preceded the bubbler, which contained 0.1 N KOH (pH 13) at an initial maximum volume of 15 mL and a final minimum volume of 10 mL. A complete HCN sample is a bubbler water fraction and a particulate fraction.

CEM was performed onsite to give immediate feedback on several light permanent gases. As shown in Figure 2, the CEM probe used port 1 and a 75-ft heated umbilical cord to carry the gases out of the exclusion zone to the mobile laboratory. Onsite analyses by CEM were performed on O_2 and CO_2 using EPA Method 3A (EPA 1996a), NO_x using EPA Method 7E (EPA 1996b), CO using EPA Method 10 (EPA 1996c), and THC using EPA Method 25A (EPA 1996d).
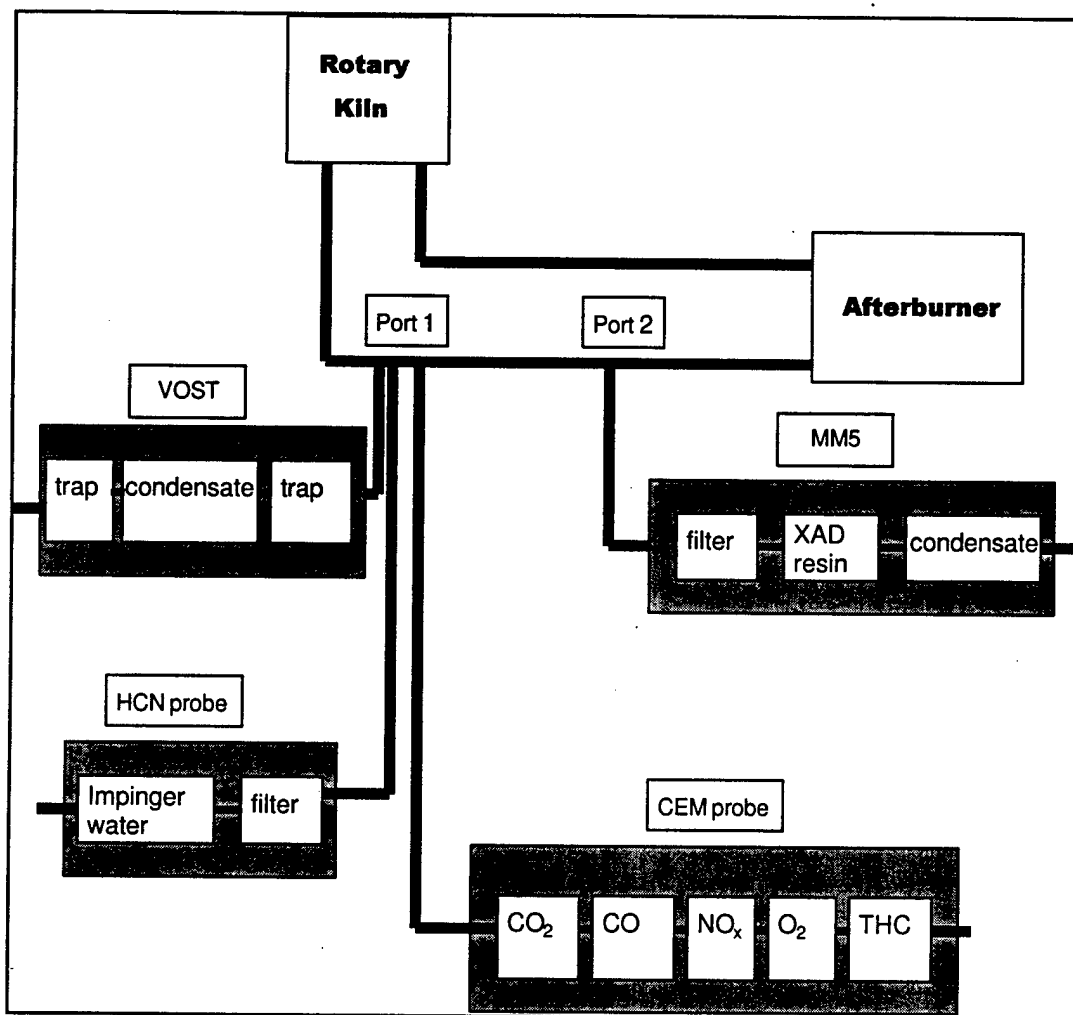
Figure 2. Port and probe configurations.

Incinerator Samples

The exact sampling times for each collected sample are listed by waste feed in Table 1. Included in the table is information on the background samples collected while the incinerator was operated with no sample feed. No trip blanks were collected during these experiments. Omitted from Table 1 are the field blanks and all CEM sampling times, as these were measured over the entire incineration event for the background run and each of the three EW burns.

Three VOC samples were taken for each incinerator waste stream. Sampling was conducted at a rate of 1 L/min for about 20 min. A field blank was collected by uncapping some traps at the incinerator site for a period of time similar to the time it takes to exchange sample cartridges in the VOST collection train. Two SVOC samples were collected for each of the incinerator feed streams. Each sample was collected over approximately half of incineration operation time for that waste feed. An SVOC field blank was collected in the same manner as the VOC field blank. All collected VOC and SVOC samples were refrigerated at 4 °C until analyzed. Three HCN samples were collected for each incineration run. Sampling occurred at a rate of 1 L/min for 1 hr. The collected sample in the impinger water bubbler was quantitatively transferred to a 20 mL vial for shipment with the filter to the analytical laboratory.

Table 1. Sampling periods for each waste feed.

Day	Waste Feed	Sample Type	Sample Number	Collection Time (min)
1	None (Background Sample)	VOC	1	60
		SVOC	1	120
		HCN	1	75
2	NC fines	VOC	1	20
			2	23
			3	20
		SVOC	1	377
			2	310
		HCN	1	123
			2	88
			3	61
3	NG slums	VOC	1	22
			2	22
			3	20
		SVOC	1	352
			2	314
		HCN	1	60
			2	60
			3	60
4	AA2	VOC	1	20
			2	20
			3	30
		SVOC	1	283
			2	279
		HCN	1	60
			2	60
			3	60

Analysis Methodology

All collected samples and blanks were spiked with laboratory standards prior to analysis. The chosen compounds were selected from a list of recommended compounds in the respective EPA methods (EPA, December 1996 and January 1998). Listed in Tables 2 and 3 are the laboratory standards for the volatile and semi-volatile samples, respectively. The adsorbent traps of the VOST were treated as a single sample unit to reduce the number of analytical runs.

Table 2. Laboratory standards for QA/QC of VOC GC/MS analysis.

Compound	Amount (ng)
1,1-Dichloroethene	250
Trichloroethylene	250
Fluorobenzene	250
Chlorobenzene	250
Chlorobenzene-d5	250
1,4-Dichlorobenzene-d4	250

Table 3. Laboratory standards for QA/QC of SVOC GC/MS analysis.

Compound	Concentration
2-Fluorophenol	20 ppm
Nitrobenzene-d5	20 ppm
Naphthalene-d8	10 ppm
2-Fluorobiphenyl	10 ppm
2,4,6-Tribromophenol	10 ppm
Phenanthrene-d10	10 ppm
PCB 65	10 ppb

The VOC collected by the adsorbent traps of the VOST were recovered using solvent extraction with GC grade methylene chloride. The VOC in the condensate was retrieved from the impinger water samples by the purge and trap technique using a Tekmar LSC 2000 (Tekmar-Dohrmann, Cincinnati, OH). Both VOC samples types were analyzed on a Saturn I gas chromatography/mass spectrometry (GC/MS) unit (Varian, Inc., Walnut Creek, CA). Separation was achieved using a DB624 column (J&W Scientific, Folsom, CA), 30 m x 0.25 mm x 1.4 μm film thickness, using a gradient oven program. The mass spectral scan range was from 60 to 260 amu. Details of the recovery and analysis procedure can be obtained from EPA Method 5041A (EPA, December 1996).

Both the XAD resin material and filter of the SVOC samples were transferred to a Soxhlet apparatus for extraction by GC grade methylene chloride. The condensate was treated by sequential acidic and caustic extraction into GC grade methylene chloride and then combined to make a single extract. All SVOC ex-

tracts were concentrated to a volume of 0.75 mL using a Turbo Vap 500 (Zymark Corp., Hopkinton, MA) before analysis on a Varian Saturn I GC/MS. Separation was achieved on a DB17MS column (J&W Scientific), 30 m x 0.25 mm x 0.25 μm film thickness, using a gradient oven program. The mass spectral scan range was from 50 to 450 amu. Details of the recovery and analysis procedure can be obtained from EPA Method 0010 (EPA 1986b) and EPA Method 8270D (EPA 1998).

The HCN water samples were transferred to a 20-mL volumetric flask for analysis, and the filters were extracted with 0.1 M KOH. Analysis was conducted with an Orion EA940 cyanide electrode (Orion Corp., Beverly, MA) as described in NIOSH Method 7904 (NIOSH 1994).

Various analytical methods were used for CEM. Both CO and CO_2 were detected by nondispersive infrared for the detection ranges of 0 - 1000 ppm and 0 - 20% by volume, respectively (EPA 1996c, 1996a). Chemiluminescence was used for the detection of NO_x (0 - 500 ppm) (EPA 1996b) while the paramagnetic property of O_2 was used for its detection (0 - 25% by volume) (EPA 1996a). A heated flame ionization analyzer provided the detection of THC (0 – 1000 ppm) (EPA 1996d). Each analyzer was zeroed and spanned with gas standards before and after each test period.

3 Results and Discussion

VOC Analysis

Sample Blanks – VOC

One field blank was collected for the VOC samples. Figure 3 shows the chroma-
togram of the adsorbate fraction of the VOC field blank. The condensate fraction
showed only the laboratory standards and is not presented here. The best li-
brary match of the mass spectra for the numbered peaks in Figure 3 is listed in
Table 4. All laboratory standards are observed except fluorobenzene and chloro-
benzene, but dichloroethene is seen twice. These standards are labeled with an
"s" on the figure and in the table. None of the surrogate standards are observed.
One peak is due to column bleed and is labeled "Si" on Figure 3.
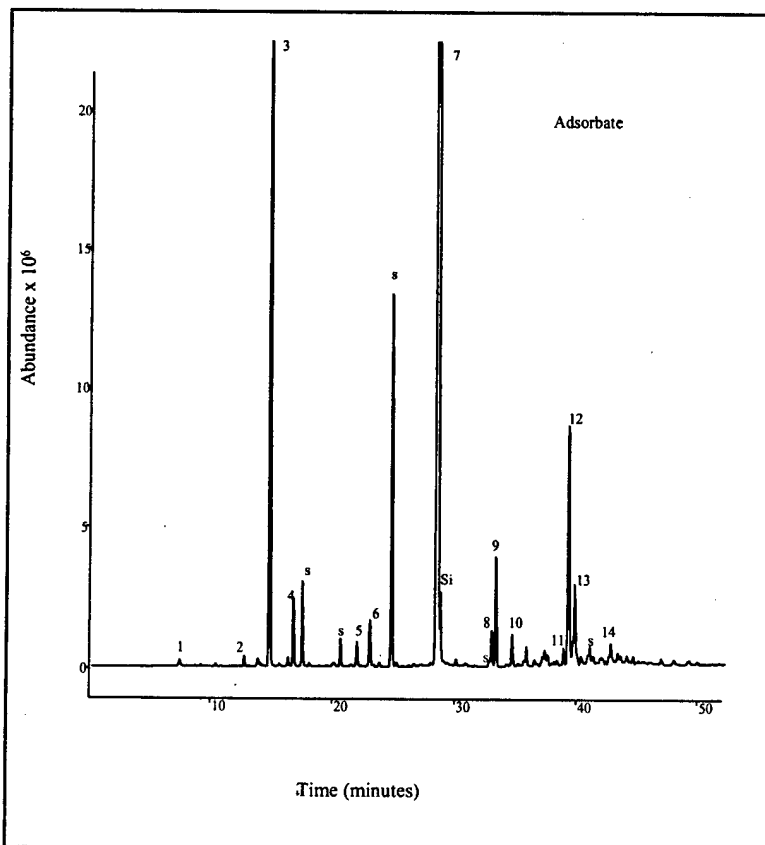
Figure 3. VOC field blank.

Table 4. Identification of compounds in VOC field blank (Figure 3).

Peak	Identification	Major Ions
1	Chlorofluorocarbon	101 85
2	Chlorofluorocarbon	117 101 85
3	Chlorofluorocarbon	151 116 101 85
4	Unidentified	132 97 84
s	Dichloroethene	96 61
s	Dichloroethene	96 61
5	Chlorofluorocarbon	117 97 82 61
6	Benzene	78
s	Trichloroethylene	96 75 63
7	Toluene	92 91
s	Chlorobenzene-d5	117 82
8	Xylene	106 91 77 65
9	Dimethylbenzene	106 91 77 65
10	Ethylbenzene	106 91 77 65
11	1-Ethyl-2-methylbenzene	120 105 91
12	Benzaldehyde derivative	155 105 77
13	1-Methyl-2-(1-methylethyl)benzene	134 119 103 91 78
s	1,4-Dichlorobenzene-d4	150 115 105 91 78
14	Hydroxybenzaldehyde	148 133 119 105 91 77 65

Of the major peaks, only peak 4 is left unidentified because a reasonable match to any library mass spectrum was unattainable. The largest peak (7) in the chromatogram is identified as toluene. Benzene (6) elutes before toluene as do all halogenated aliphatic compounds. These halogenated compounds (1, 2, 3, 5) are labeled as chlorofluorocarbons, and the likely source is refrigeration. Several of these same compounds also appear in the laboratory blanks (not shown) further supporting refrigeration as a contamination source. The analysis method specifically warns of the possibility of contamination from seepage through the seal during refrigeration. Aromatic compounds appear after toluene. Most of these peaks (8-11, 13) are identified as alkyl benzene compounds. The listed identifications in Table 4 are representative of the likely species, but are not definitively assigned due to the indistinguishable mass spectra among isomers. Correct identification of these alkyl benzene compounds would require retention data from standards analyzed under identical conditions. Peak 12 has strong daughter ions 105 and 77, leading to a search result of benzaldehyde. However, the mass spectra do not correlate with regard to relative ion ratios, and ion 155 is clearly present in the mass spectrum of peak 12; therefore, this peak is referred to as a benzaldehyde derivative. Peak 14 is hydroxybenzaldehyde.

Incineration Background Samples – VOC

Since this VOC sample was collected from the incinerator during operation but
without an input waste feed, these data will provide a baseline for comparison to
other results and allow the determination of by-products that may be evolving
due to two separate mechanisms. The first mechanism is the production of spe-
cies from combustion of the natural gas itself. The second mechanism is the pos-
sible release of contaminants from the internal kiln surfaces deposited during
previous incineration runs.

The chromatograms of the adsorbate fraction and the condensate fraction of the
VOC background sample are shown in Figures 4(a) and 4(b). The numbering of
peaks is consistent between the upper and lower chromatograms. Table 5 identi-
fies all the labeled peaks from both the adsorbate and the condensate as well as
the major observed ions from each peak. Five of the laboratory standards are
observed in these samples; dichloroethene appears twice and chlorobenzene is
not observed. One of the dichloroethane peaks is probably another chlorinated
compound with a similar mass spectrum. Fluorobenzene, chlorobenzene-d5, and
dichlorobenzene-d4 are easier to see in the condensate fraction while the di-
chloroethene and trichloroethylene appear in the adsorbate fraction. Several
peaks (4, 6, 7) provide little clue as to their classification. Both toluene (9) and
benzene (8) have become more substantial in this background sample as com-
pared to the field blank, which is likely due to the difference in collection time.
It has been noted that toluene, benzene, and other larger polycyclic aromatic
compounds such as xylene (10) and alkyl benzenes (11, 15), can result from the
combustion of natural gas in a fuel rich flame (Toqan et al. 1993; Edwards 1974).
Dinitrotoluene (DNT) has been incinerated at this facility in the past and could
also contribute a source of aromatics by coating the interior of the kiln with its
by-products. For example, benzene dicarboxaldehyde (12) and 1,3-benzodioxole
(16) are new species evolving from this background sample despite the absence of
input feed. It has been shown that soot deposits can be a source of by-products
from industrial boilers long after the input waste feed has stopped (Gullett,
Touati, and Lee 2000). Peaks 1, 2, 5, 6, and 7 are other newly observed species,
but only peak 2 is roughly identified. Co-elution of compounds caused difficulty
in interpreting the mass spectrum for peak 1. Since the lower limit of the mass
scan range was 60 amu, fragment peaks were not collected, thus causing inter-
pretation and identification problems.

Few VOCs are found in the condensate fraction of the background sample com-
pared to the adsorbate fraction. Thus, little breakthrough occurred during the
background sample collection. The largest peak (4) in the condensate sample is
unidentified. Both toluene and benzene are present, although the benzene con-

centration is, as usual, far less than toluene and is barely observable on this scale.
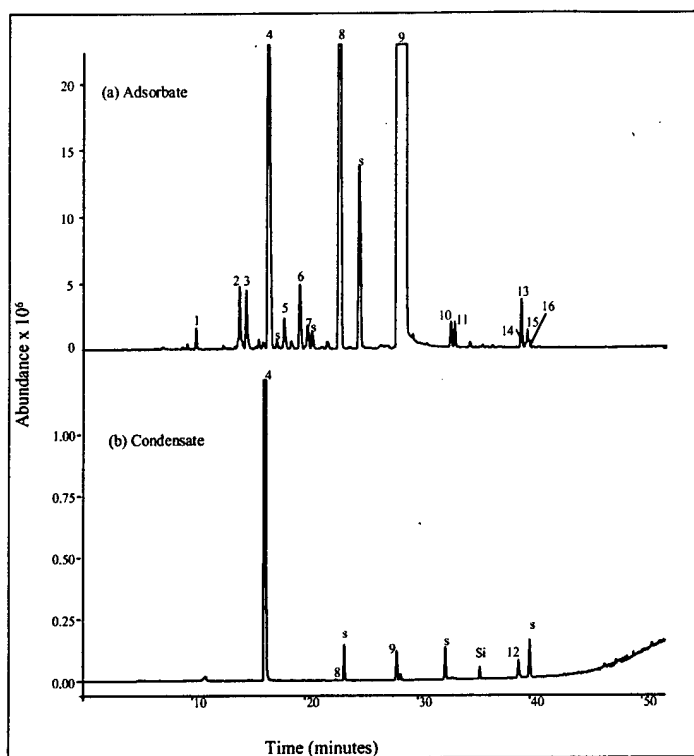
Figure 4. VOC incinerator background —
(a) adsorbate and (b) condensate.

Table 5. Identification of VOC in incineration background (Figure 4).

Peak	Identification	Major Ions
1	Co-eluting compounds	128 103 78 63 and 116 105 91 80
2	1H-Pyrazole or 1H-Imidazole	69 68 67
3	Chlorofluorocarbon	151 116 101 85 66
4	Unidentified	132 97 83 66
s	Dichloroethene	96 61
5	C_5H_6	66 65 63
6	Unidentified	81
7	Unidentified	82 69
s	Dichloroethene	96 61
8	Benzene	78
s	Fluorobenzene	96 70
s	Trichloroethylene	130 95 82 60
9	Toluene	92 91
s	Chlorobenzene-d5	117 82
10	Xylene	106 91 77 65
11	Ethylbenzene	106 91 77 65
12	Benzenedicarboxaldehyde	134 105 77
13	Benzaldehyde derivative	155 105 77
14	$C_{10}H_{16}$	136 108 93 77 65
15	Alkylbenzene	134 119 103 91 77 65
16	1,3-Benzodioxole	121 91 77 63
s	1,4-Dichlorobenzene-d4	150 115 78

NC Fines Samples – VOC

Three VOC samples collected during the incineration of NC fines resulted in the chromatograms in Figure 5 for the adsorbate fractions and Figure 6 for the condensate fractions. Reproducibility is excellent among the three samples for both fractions. Both fractions exhibit nearly the same number of peaks. Tables 6 and 7 identify the labeled peaks in Figure 5 and Figure 6, respectively. The early eluting laboratory standards tend to appear in the adsorbate fractions while the later eluting standards appear in the condensate fractions. Chlorobenzene is absent as are all the surrogate standards. These laboratory standards are denoted with an "s" in Figures 5 and 6 and Tables 6 and 7. While Figure 5 shows good reproducibility among the detected analytes, it also shows the difficulties in spiking with the volatile laboratory standards, dichloroethene and trichloroethylene, as these peaks widely differ in intensity for these three samples.

Compounds in the adsorbate fraction that also appear in the background samples are benzene (3), toluene (4), and other alkylbenzenes (6 – 11). The remaining peaks (1, 2, 5, 12, and 13) originate from the NC fines since they are absent from the background sample. Peaks 1 and 2 are closely related in structure because of their nearly identical mass spectrum. Peak 5 is proposed to be a cyclic hydrocarbon while peak 12 is unidentified.

Figure 5. VOC from NC fines incineration: adsorbate fractions.

Table 6. Identification of compounds present in the VOC NC fines adsorbate fraction (Figure 5).

Peak	Identification	Major Ions
1	Small hydrocarbon	110 96 83 70
2	Small hydrocarbon	110 96 85 69
s	Dichloroethene	96 89 72 61
3	Benzene	78
s	Trichloroethylene	132 130 95
4	Toluene	92 91
5	Cyclic hydrocarbon	126 111 97 83 69
6	Xylene	106 91 65
7	Dimethylbenzene	106 91 65
8	Ethylbenzene	106 91 65
9	Methylethylbenzene	120 105 91 79
10	Propylbenzene	120 91 65
11	Ethylmethylbenzene	120 105 91 65
12	Unidentified	117 105 91 71
13	$C_{10}H_{16}$	136 128 107 95 79 67
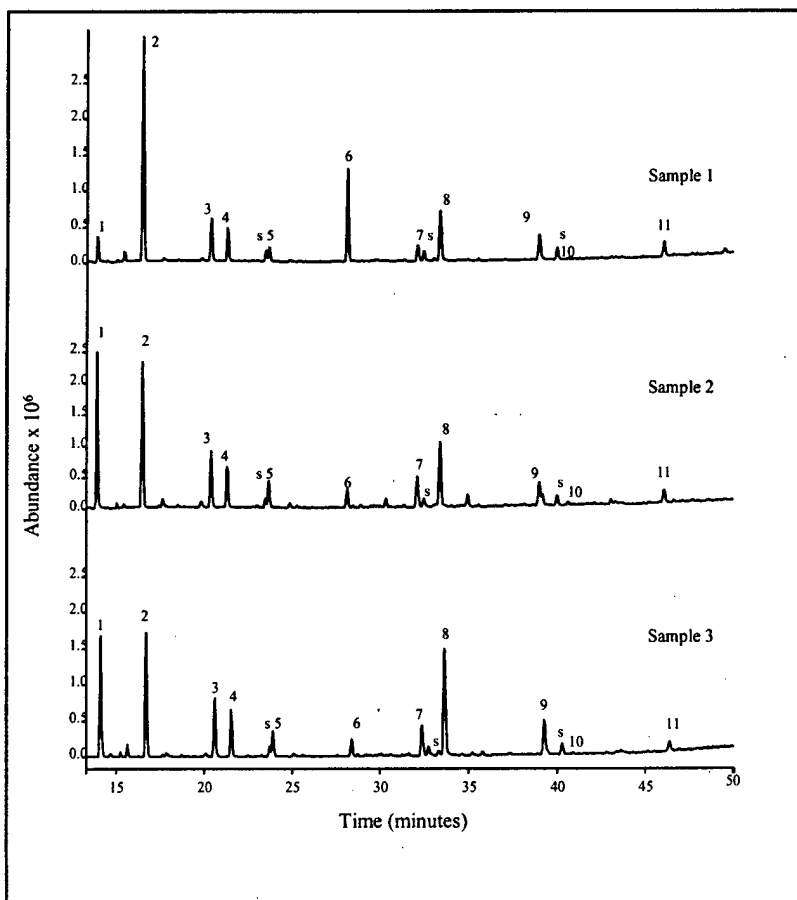
Figure 6. VOC from NC fines incineration: condensate fractions.

Table 7. Identification of compounds present in the VOC NC fines condensate fraction (Figure 6).

Peak	Identification	Major Ions
1	1H-Pyrazole or 1H-Imidazole	69 68 67
2	Unidentified	97 84
3	Unidentified	91 76 61
4	2,5-Dihydro-1H-pyrrole	70 69 68
s	Fluorobenzene	96 70
5	Dimethylcyanamide	71 70 69
6	Toluene	92 91
7	Furancarboxaldehyde	95 67
s	Chlorobenzene-d5	117 82
8	Furancarboxaldehyde	95 67
9	Benzaldehyde	105 77
s	1,4-Dichlorobenzene-d4	150 115 78
10	Benzonitrile	103 76
11	Nitrophenol	139 109 92 81 63

The condensate fraction contains mostly species with a heteroatom and an acidic hydrogen. Only toluene (6) is common to both fractions since it is present in such abundance. Peak 1, pyrazole, was also observed in the background. The remaining peaks, however, are unique to NC fines. Peaks 2 and 3 were not identified through a library search. Although identification is not completely certain because of the few ions present in the mass spectra, peaks 4 and 5 appear to be 2,5-dihydro-1H-pyrrole and dimethylcyanamide. The remaining peaks are furancarboxaldehyde (7 and 8), benzaldehyde (9), benzonitrile (10), and nitrophenol (11).

NG Slums Samples – VOC

The chromatograms generated from the three VOC samples collected during the incineration of NG slums are shown in Figures 7 and 8 for the adsorbate and condensate fractions, respectively. The collection time for each sample was nearly the same; therefore, little overall variation in the detected species among the three samples was observed. Any difference among the chromatograms of the samples was attributed to fluctuation in the waste feed. This difference is manifested primarily in the relative ratio of peaks, especially peaks 11 through 14 in the adsorbate fraction. The condensate fractions exhibited consistent behavior among the three samples.

Tables 8 and 9 identify the labeled peaks in Figures 7 and 8. Again missing from the samples are all of the QA/QC surrogate standards and the chlorobenzene laboratory standard. All other laboratory standards are detected, split between the adsorbate and condensate. The trichloroethylene was observed to be incon-

sistent in the adsorbate fraction. The letter "s" denotes the peaks of these labo-
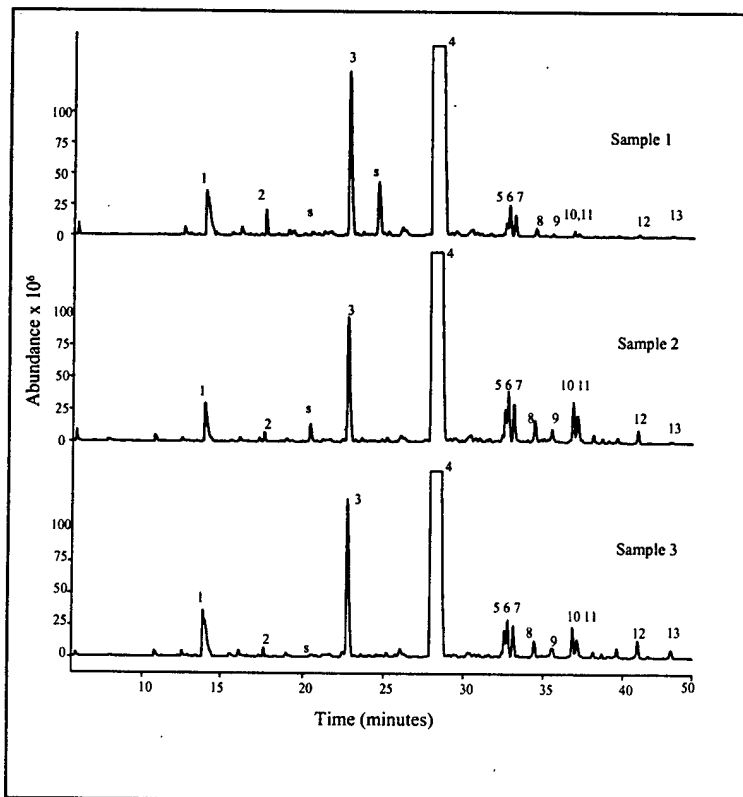ratory standards.

Figure 7. VOC from NG slums incineration: adsorbate fractions.

**Table 8. Identification of compounds present in the VOC NG slums adsorbate
fraction (Figure 7).**

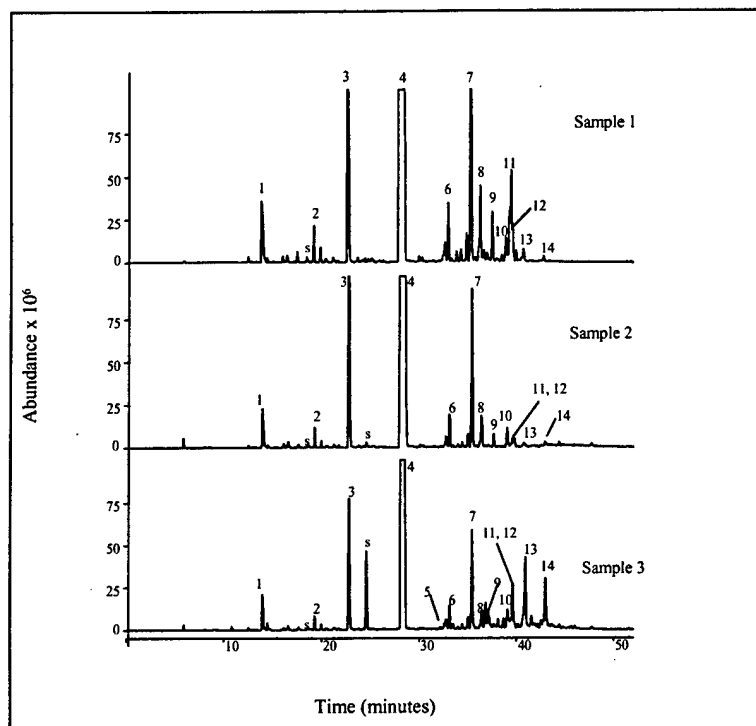| Peak	Identification	Major Ions
1	1H-Pyrazole or 1H-Imidazole	69 68 67
s	Dichloroethene	96 61
2	$C_4H_6N_2$	83 82 81
3	Benzene	78
s	Trichloroethylene	191 130 96
4	Toluene	92 91
5	Furancarboxaldehyde	95 67
6	Xylene	106 91 79 65
7	Benzaldehyde derivatives	136 121 105 91 77 65
8	Benzaldehyde derivatives	136 121 105 91 77 65
9	Benzaldehyde derivatives	136 121 105 91 77 65
10	Benzaldehyde	105 77
11	Alkylbenzene	134 119 105 91
12	Benzofuran	118 89 63
13	Unidentified	117 105 91
14	Benzaldehyde derivatives	136 121 105 91 77 65
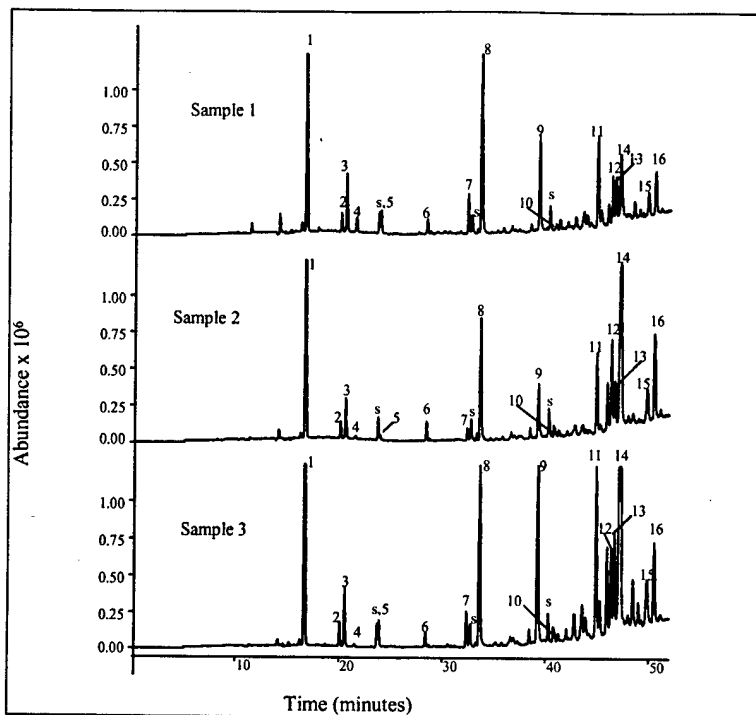
Figure 8. VOC from NG slums incineration: condensate fractions.

Table 9. Identification of compounds present in the VOC NG slums condensate fraction (Figure 8).

Peak	Identification	Major Ions
1	Unidentified	97 85
2	Unidentified	128 112 85 69
3	Unidentified	91 76 61
4	2,5-Dihydro-1H-pyrrole	70 69 68
s	Fluorobenzene	96 70
5	Dimethylcyanamide	71 70 69
6	Toluene	92 91
7	Furancarboxaldehyde	95 67
s	Chlorobenzene-d5	117 82
8	2-Furancarboxaldehyde	95 67
9	Benzaldehyde	105 77
s	1,4-Dichlorobenzene-d4	150 115 105 91 78
10	Benzonitrile	103 76
11	$C_{10}H_{16}O$	152 137 108 95 81 67
12	Nitrophenol	139 122 109 92 81
13	$C_{10}H_{16}O$	152 137 108 95 81 67
14	Unidentified	136 121 118 95
15	Methyl nitrophenol	153 135 107 95 77
16	Methyl nitrophenol	153 135 107 95 77

In the adsorbate fractions, benzene (3) and toluene (4) are again dominant. Some background peaks such as alkylbenzenes (6 and 11) and pyrazole (1) are present, but the remaining peaks are due to incineration of NG slums. Identification of peaks 2 and 13 are unknown. Peaks 7, 8, 9, and 14 have identical mass spectra. Because of the mass peaks at 105 and 77, which are also present in

benzaldehyde, and mass peak 91, these four peaks (7, 8, 9, and 14) are incompletely identified as benzaldehyde derivatives. Furancarboxaldehyde (5), benzaldehyde (10), and benzofuran (12) were also detected.

The condensate fractions have a comparable number of peaks to the adsorbate fractions with a few common species: toluene (6), furancarboxaldehyde (7), and benzaldehyde (9). The condensate fraction tends to collect polar compounds with an active hydrogen atom. Many peaks are not identified and two of these, peaks 1 and 3, are also produced by incineration of NC fines (see Table 7). The pyrrole (4) compound, dimethylcyanamide (5), furancarboxaldehyde (7 and 8), benzonitrile (10), and nitrophenol (12) were also observed in the NC fines samples. Two of the peaks, 11 and 13, have identical mass spectra, but can only be classified as oxygen-containing hydrocarbons. Methyl nitrophenol (15 and 16) appears twice in the NG slums condensate fraction.

AA2 Samples — VOC

Three VOC samples were collected during the incineration of AA2. Differences were observed among the chromatograms of the three adsorbant samples, which are shown in Figure 9. The concentration of by-products was higher in the last sample compared with the first two samples. This difference could be due either to sample handling in the laboratory or to fluctuations in the sample feed over this collection period. This pattern, however, did not carry over to sample 3 of the condensate fractions as shown in Figure 10 where, at least from 0 to 40 minutes, the small components in sample 3 appear to be smaller than the same peaks in samples 1 and 2. The data collection for the sample 3 condensate fraction was interrupted after 40 minutes. The reason for the interruption was instrument failure, but up to 40 minutes, the three samples were nearly identical.

Identifications of labeled peaks in Figure 9 are listed in Table 10 while the condensate peaks in Figure 10 are listed in Table 11. An "s" in either figure or table indicates a laboratory standard. None of the QA/QC surrogate standards were observed in either fraction. Five of the six laboratory standards were observed in either the condensate or the adsorbate samples. Dichloroethene was observed only in the adsorbate fraction of the first sample, but is unlabeled because its small peak is not visible on the scale.

Figure 9. VOC from AA2 incineration: adsorbate fractions.

Table 10. Identification of compounds present in the VOC AA2 adsorbate fraction (Figure 9).

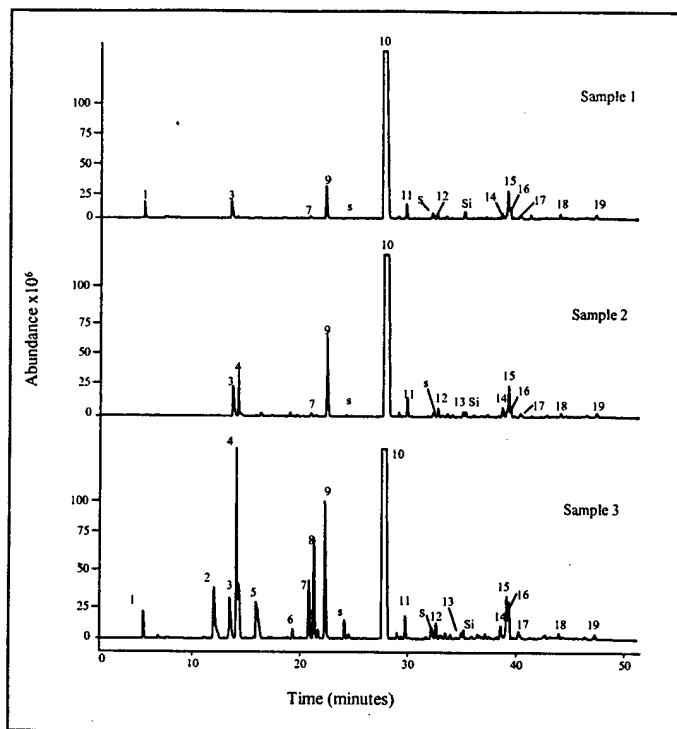| Peak	Identification	Major Ions
1	Unidentified	Saturated ms
2	Chlorofluorocarbon	117 101 91 70
3	C_5H_8	68 67 66
4	Chlorofluorocarbon	132 117 101 85 73
5	Unidentified	83 + saturated cluster
6	Chlorofluorocarbon	117 85 71
7	Chlorofluorocarbon and C_8H_{16}	118 85 83 and 115 75 68
8	Trichloroethane	133 117 97 83
9	Benzene	78
s	Trichloroethylene	130 95 60
10	Toluene	92 91
11	Sulfur compound	232 116 61
s	Chlorobenzene	112 77
12	Xylene	106 91
13	Unidentified	136 121 105 91 77 65
14	Benzaldehyde derivative	155 105 77
15	Alkylbenzene	134 119 91
16	Benzofuran	118 89 63
17	Benzonitrile	103 76
18	Paraffin	170 85 71
19	Naphthalene	128 102 85 71
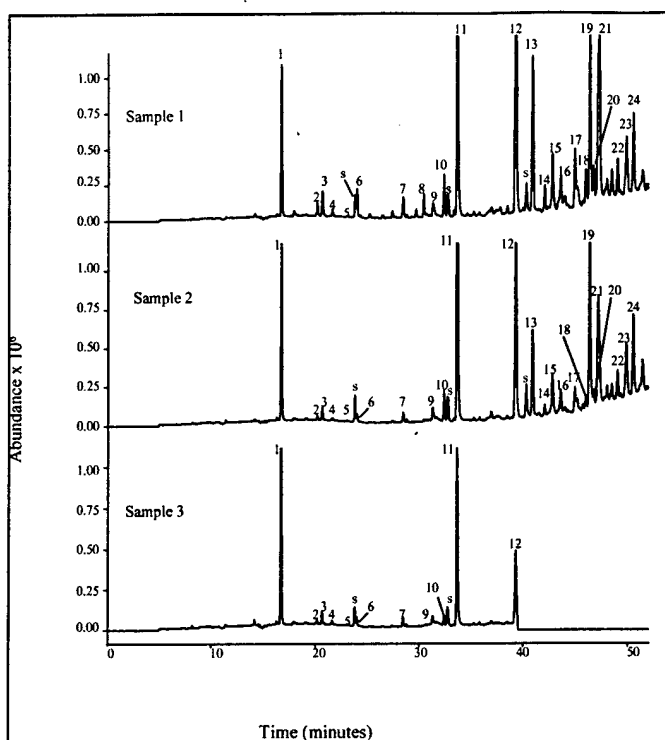
Figure 10. VOC from AA2 incineration: condensate fractions.

Table 11. Identification of compounds present in the VOC AA2 condensate fraction (Figure 10).

Peak	Identification	Major Ions
1	Unidentified	97 84
2	Unidentified	128 112 85 69
3	Unidentified	76 61
4	2,5-Dihydro-1H-pyrrole	70 69 68
5	Benzene	78
s	Fluorobenzene	96 70
6	Dimethylcyanamide	71 70 69
7	Toluene	92 91
8	Unidentified	117 73 61
9	2(5H)-Furanone	84
10	Furancarboxaldehyde	95 67
s	Chlorobenzene-d5	117 82
11	Furancarboxaldehyde	96 95 67
12	Benzaldehyde	106 105 77
s	1,4-Dichlorobenzene-d4	150 115 78
13	Benzonitrile	103 76
14	$C_{11}H_{18}$	152 137 93 79
15	Hydroxybenzaldehyde	121 104 93 76 65
16	Alkylbenzaldehyde	120 105 91 77
17	$C_{10}H_{18}O$	139 121 107 93 81 67
18	Oxygenated compound	134 119 105 91 79
19	Nitrophenol	139 109 81 63
20	$C_{10}H_{16}O$	152 139 108 95 81 67
21	$C_{10}H_{16}$	136 121 110 95 77 67
22	Alkylbenzaldehyde	148 133 119 105 91 77
23	Methyl nitrophenol	153 135 107 91 77 65
24	Methyl nitrophenol	153 135 123 105 95 77

A comparison between the AA2 VOC adsorbate fraction and the background VOC fraction (Figure 4) shows many common aromatic species and chlorofluorocarbons; primarily benzene (9), toluene (10), xylene (12), the benzaldehyde derivative (14), and alkyl benzene (15). Peaks 1, 3, 5, and 13 are unidentified and are due to the incineration of AA2. In addition, benzofuran (16), benzonitrile (17), paraffin (18), and naphthalene (19) also originate from AA2. The peak labeled "Si" is due to column bleed.

The number of incinerator by-products from AA2 found in the condensate is greater than the number found in the adsorbate fraction. As expected, these by-products have a heteroatom and an active hydrogen atom. Examination of the chromatograms (Figure 10) shows that the run time should have been extended. It appears that more peaks may yet have eluted from the column. Almost all of these peaks originate from the AA2. Some of the same compounds are also found in the NC and NG samples presented earlier. Some of the later eluting peaks are not identified (16 - 18, 20 - 22) but include oxygen-containing compounds, alkylbenzaldehydes, and hydrocarbons.

SVOC Analysis

Sample Blanks – SVOC

One field blank was collected for the SVOC samples. The chromatograms are shown in Figure 11. The results from examination of the mass spectra of the larger peaks are presented in Table 12. The chromatogram of the adsorbate fraction displays numerous peaks. Many of these peaks are the laboratory and surrogate standards, which are labeled with the letter "s." Note that all SVOC standards are observed. One prominent phthalate, labeled as "p," is common to all fractions. Peak 1 appears to be an olefinic hydrocarbon, but all other numbered peaks indicate the presence of aromaticity. Notable by its absence is toluene, which overwhelmed all VOC samples. Small amounts of toluene are observed in other SVOC samples shown below. This result indicates that huge amounts of toluene are probably not present at the incinerator but rather that this was a laboratory or method contaminant. The condensate and the filtrate chromatograms contain only the standards. The few additional peaks in the filtrate are phthalates and siloxanes, possibly from the filter material.
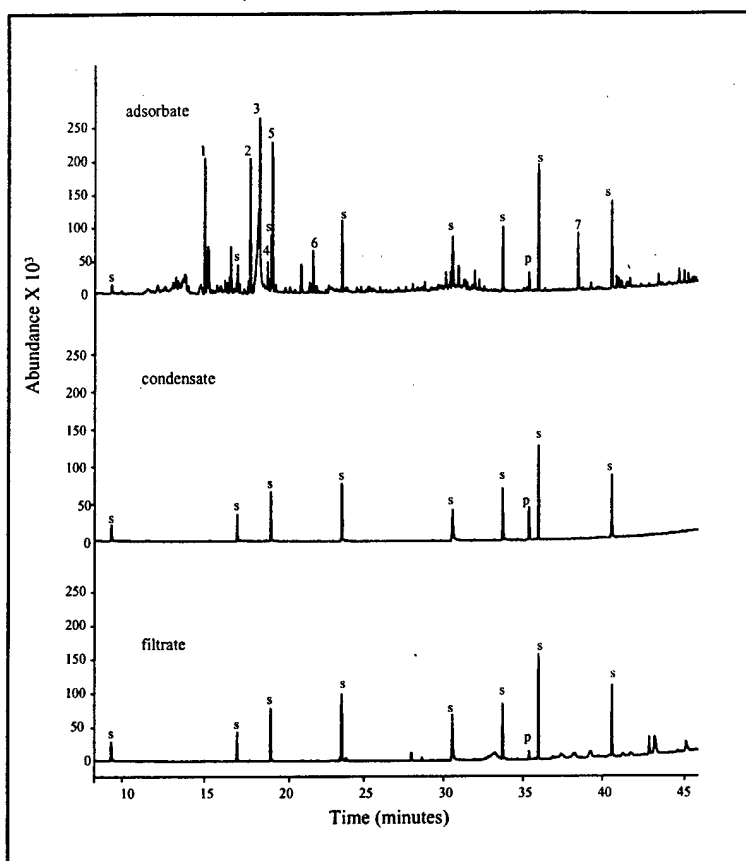
Figure 11. SVOC field blank.

Table 12. Identification of compounds present in the SVOC field blank (Figure 11).

Peak	Identification	Major Ions
s	2-Fluorophenol	112 92 83 63
1	$C_{10}H_{12}$	132 117 102 91
s	Nitrobenzene-d5	128 98 82 70
2	Triethylbenzene	162 147 133 115 104 91 78
3	Benzoic Acid	122 105 77 51
4	Ethylbenzaldehyde	133 119 105 91 77
s	Naphthalene-d8	136 108 76
5	Naphthalene	128 102
6	N-Methylbenzamide	135 105 91 77 55
s	2-Fluorobiphenyl	172 152 133 98 85
s	2,4,6-Tribromophenol	332 250 222 141
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
7	Diphenyl ethanedione	210 105 77 51
s	p-Terphenyl-d14	244 212 160

Incineration Background Samples – SVOC

An SVOC sample was collected from the incinerator as it operated for 1 day without input waste feed. Similar to the VOC data, this sample provided a subset of compounds that evolve as background species. Figure 12 shows the chromatograms of the SVOC background sample. Examination of Table 13 shows that most of the peaks are the laboratory and surrogate standards denoted by "s." All fractions are very similar to the corresponding fraction of the field blank (Figure 11). The only new by-product in the background sample is the large amount of squalene (peak 6). Again, the condensate fraction contains only the standard compounds, while the filtrate contains an abundance of siloxanes and phthalates.
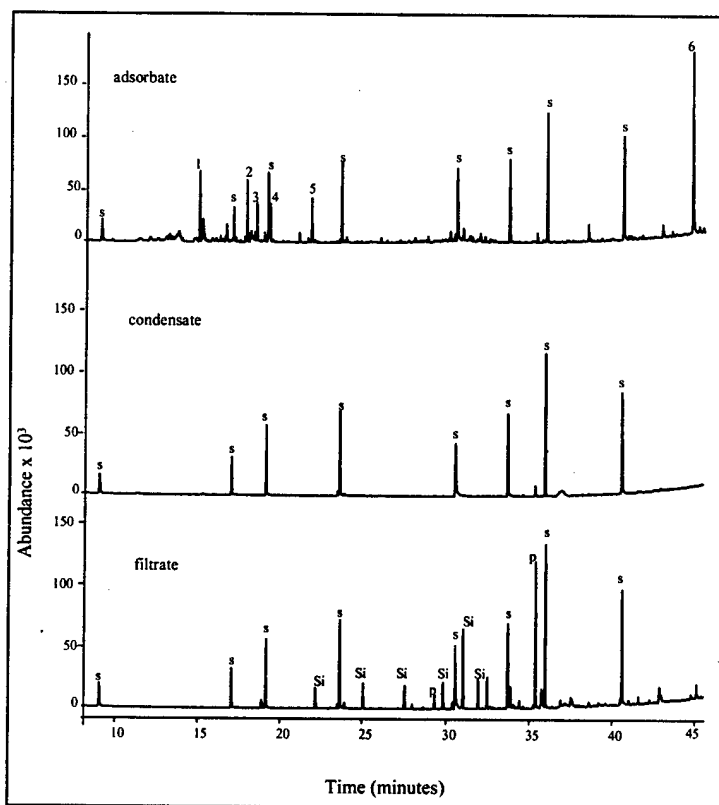
Figure 12. SVOC incinerator background.

Table 13. Identification of compounds present in the SVOC incinerator background
(Figure 12).

Peak	Identification	Major Ions
s	2-Fluorophenol	112 92 83 63
1	$C_{10}H_{12}$	132 117 91
s	Nitrobenzene-d5	128 98 82 70
2	Tetrahydronaphthalene	177 132 115 104 91 78
3	Triethylbenzene	162 133
s	Naphthalene-d8	136 108 76
4	Naphthalene	128 102
5	N-Methylbenzamide	135 105 91 77
s	2-Fluorobiphenyl	172 152 133 98 85
s	2,4,6-Tribromophenol	332 250 222 141
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
s	p-Terphenyl-d14	244 212 160
6	Squalene	341 231 189 135 121 107 95 81 69

NC Fines Samples – SVOC

Two semivolatile samples were collected during the incineration of NC fines.
The chromatograms from GC/MS analysis are shown in Figures 13, 14, and 15
for the adsorbate, condensate, and filtrate fractions, respectively. Qualitatively,
both samples appear nearly identical. All peaks denoted with the letter "s" are
the QA/QC standard compounds, which were found in all fractions of both sam-
ples.

Figure 13. SVOC from NC fines incineration: adsorbate fractions.
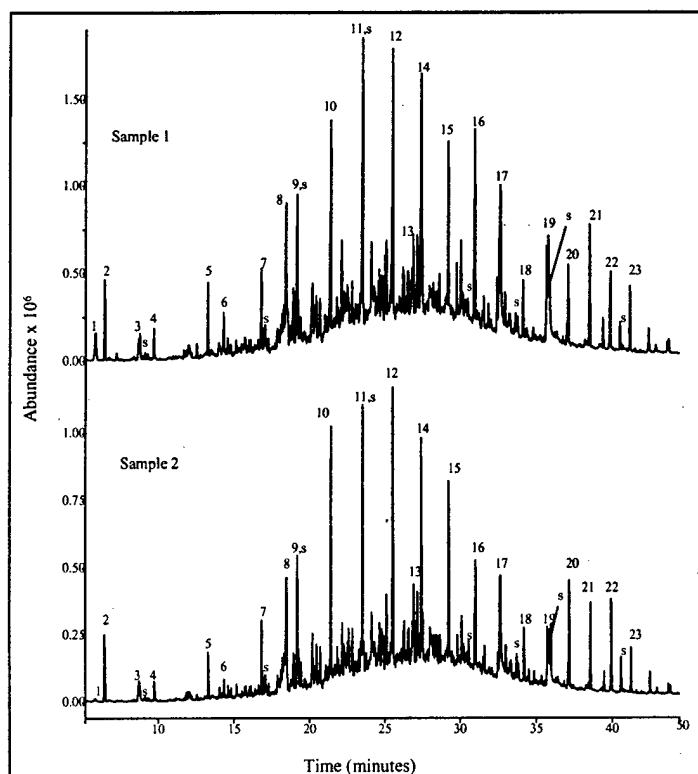
Table 14. Identification of compounds present in the SVOC NC fines adsorbate fraction (Figure 13).

Peak	Identification	Major Ions
1	Toluene	91
2	Chloroform	85 83
3	4-Hydroxy-4-methyl-2-pentanone	116 98 83 59
s	2-Fluorophenol	112 92 83 63
4	Furancarboxaldehyde	97 96 95
5	Benzaldehyde derivative	155 105 77 51
6	Hydrocarbon	99 85 71 57
7	Hydrocarbon	99 85 71 57
s	Nitrobenzene-d5	128 98 82 70
8	Benzoic acid and Ethylbenzaldehyde	122 105 77 51 and 133 119 105 91 78
9	Hydrocarbon	99 85 71 57
s	Naphthalene-d8	136 108 76
10	Hydrocarbon	99 85 71 57
11	Hydrocarbon	99 85 71 57
s	2-Fluorobiphenyl	172 152 133 98 85
12	Hydrocarbon	99 85 71 57
13	Di-n-propyladipate	230 171 142 129 111
14	Hydrocarbon	99 85 71 57
15	Hydrocarbon	99 85 71 57
s	2,4,6-Tribromophenol	332 250 222 141
16	Hydrocarbon	99 85 71 57
17	Hydrocarbon	99 85 71 57
s	Phenanthrene-d10	188 160 132 94 80
18	Hydrocarbon	99 85 71 57
19	Hydrocarbon	99 85 71 57
s	PCB	292 255 220 184 150 110
20	Hydrocarbon	99 85 71 57
21	Hydrocarbon	99 85 71 57
22	Hydrocarbon	99 85 71 57
s	p-Terphenyl-d14	244 212 160
23	Hydrocarbon	99 85 71 57

Figure 14. SVOC from NC fines incineration: condensate fractions.

Table 15. Identification of compounds present in the SVOC NC fines condensate fraction (Figure 14).

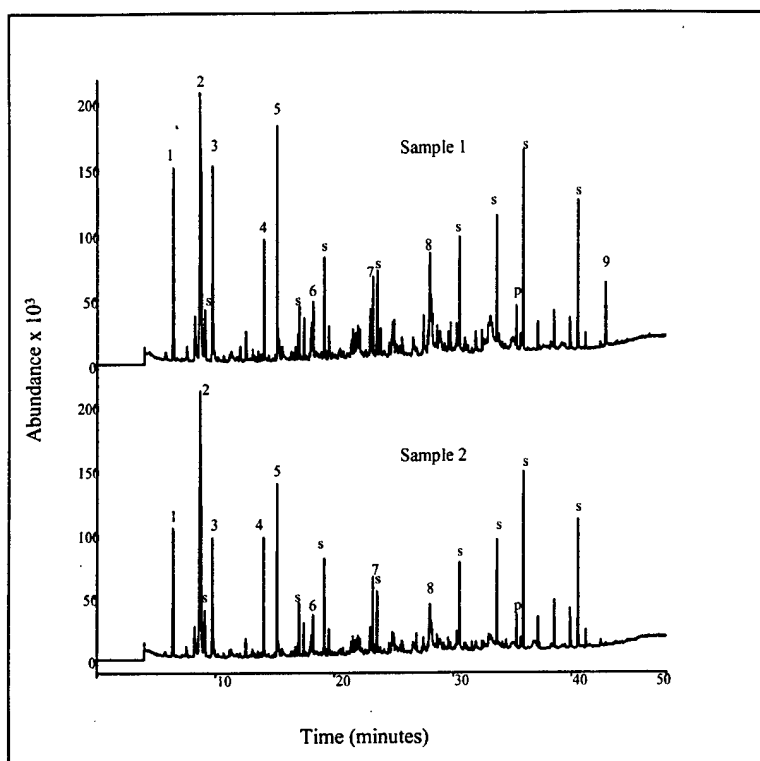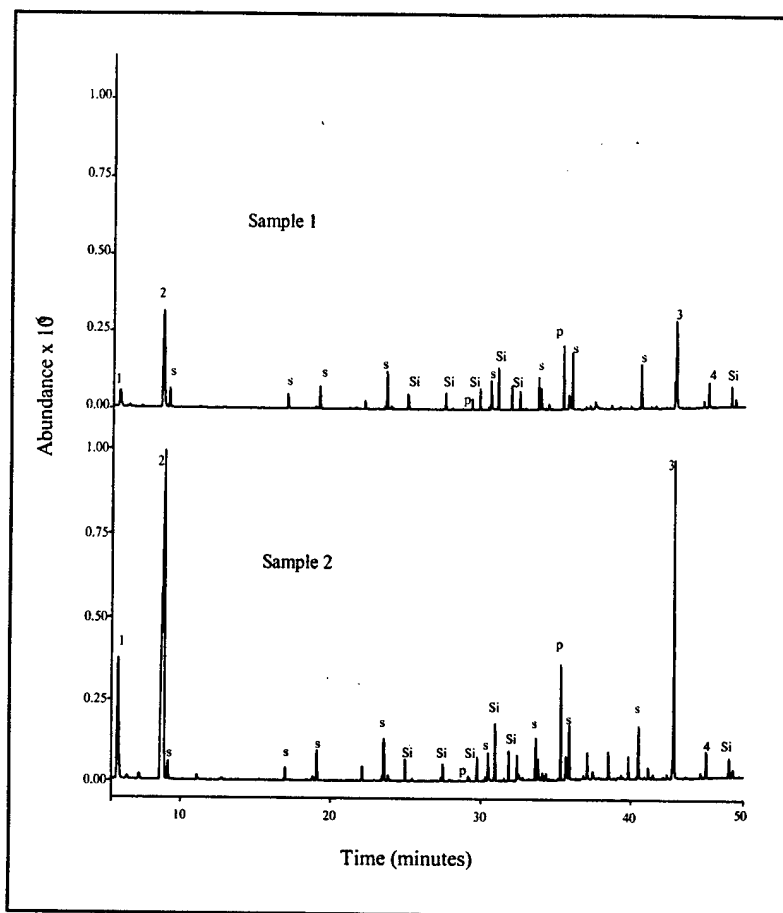| Peak	Identification	Major Ions
1	Chloroform	85 83
2	4-Hydroxy-4-methyl-2-pentanone	116 98 83 59
s	2-Fluorophenol	112 92 83 63
3	1,5-Dimethyl-1H-pyrazole	95 67
4	$C_8H_{18}O$	98 84 55
5	1H-Imidazole-2-carboxaldehyde	96 68
s	Nitrobenzene-d5	128 98 82 70
6	Benzoic acid and Dihydroxytoluene	122 105 77 51 and 123 95 67
s	Naphthalene-d8	136 108 76
7	Triacetin	159 145 115 103 74
s	2-Fluorobiphenyl	172 152 133 98 85
8	$C_9H_{18}O_3$	175 147 117 103 73 59
s	2,4,6-Tribromophenol	332 250 222 141
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
s	p-Terphenyl-d14	244 212 160
9	1,2-Benzenedicarboxylic acid, diisooctyl ester	279 167 149

Figure 15. SVOC from NC fines incineration: filtrate fractions.

Table 16. Identification of compounds present in the SVOC NC fines filtrate fraction (Figure 15).

Peak	Identification	Major Ions
1	Toluene	91
2	4-Hydroxy-4-methyl-2-pentanone	116 98 83 59
s	2-Fluorophenol	112 92 83 63
s	Nitrobenzene-d5	128 98 82 70
s	Naphthalene-d8	136 108 76
s	2-Fluorobiphenyl	172 152 13 98 85
s	2,4,6-Tribromophenol	332 250 222 141
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
s	p-Terphenyl-d14	244 212 160
3	1,2-Benzenedecarboxylic acid diisooctyl ester	279 167 149
4	1,2-Benzenedicarboxylic acid ester	249 167 149

Mass spectra for the adsorbate peaks are listed in Table 14. The dominant pattern observed in the adsorbate fractions is the repetitive long chain hydrocarbons present in the antifoaming compound. Starting at peak 6 through peak 23 (excluding peaks 8 and 13), each successive hydrocarbon peak differs by an additional methylene unit. Unfortunately, the molecular ions are not observed in the

mass spectra for these peaks and unambiguous identification of these compounds is only possible by injection of the appropriate standards. The additional compounds contributing to the chromatographic hump are branched chain compounds, olefins, and naphthenes likely present in the surfactant. Few compounds are produced from the incomplete combustion of NC: hydroxymethylpentanone (3), furancarboxaldehyde (4), benzoic acid (8), and ethyl benzaldehyde (8). Chloroform is probably a laboratory contaminant, since the incinerator burns no chlorine-containing wastes. Interestingly, di-n-propyladipate (13) was found among the hydrocarbon peaks. While this compound is a component of AA2, it is unexpected in NC fines.

The condensate fraction (Figure 14) is less complex than the adsorbate fraction. Identifications for the more abundant peaks are listed in Table 15. None of the antifoaming hydrocarbons are retained in the condensate water. Triacetin appears at peak 7, although it is not a constituent of NC fines. The presence of both triacetin and di-n-propyladipate in the NC fines samples may be due to cross-contamination between waste feeds at the incinerator. One argument in favor of this is that di-n-propyladipate is the largest peak present in the AA2 SVOC adsorbate fraction, and triacetin is the major peak present in the AA2 SVOC condensate fraction.

The filtrate fraction (Figure 15) is even less congested. Table 16 lists identifications of the peaks. Many of the peaks are siloxane compounds from either the filter or column bleed. The remaining peaks are similar to those already noted in the condensate fraction. Peak 2 is the small polar compound 4-hydroxy-4-methyl-2-pentanone. Both peaks 3 and 4 are carboxylic acid esters. The high effluent temperature prevents condensation of semivolatile compounds onto particulates.

Only small amounts of toluene are observed in the adsorbate and filtrate fractions. Toluene is ubiquitous in the VOC samples. Either the SVOC MM5 train collection efficiency is poor for small aromatic compounds or the high levels of toluene in the VOC samples are a result of gross laboratory contamination.

NG Slums Samples – SVOC

Figures 16 – 18 show the chromatograms of the adsorbate, condensate, and filtrate fractions, respectively, for the two SVOC samples collected during the incineration of NG slums. The different chromatograms for each fraction are virtually identical. In all fractions of both samples, QA/QC laboratory and surrogate standards were easily observed.

The adsorbate fraction has slightly more PIC than the condensate and filtrate fractions. Table 17 lists the identifications for the abundant peaks of the adsorbate fraction. The dominant peak (9) is the co-elution of a standard and tri-acetin. Similar to the results of NC fines, triacetin is expected only during AA2 incineration. The contaminant chloroform is the next prominent peak (1). Peak 14 has not been identified due to unsatisfactory mass spectrum matches with the mass spectra library. Other noteworthy peaks are furancarboxaldehyde (2), ben-zofuran (5), and methyl furancarboxaldehyde (5). Both naphthalene (8) and the alkylbenzene (3) were also observed in the background sample. Unlike the NC fines sample, the NG contributes copious amounts of nitro radical species that take part in PIC-forming reactions to produce nitroaromatic compound peaks (13, 15, and 16).
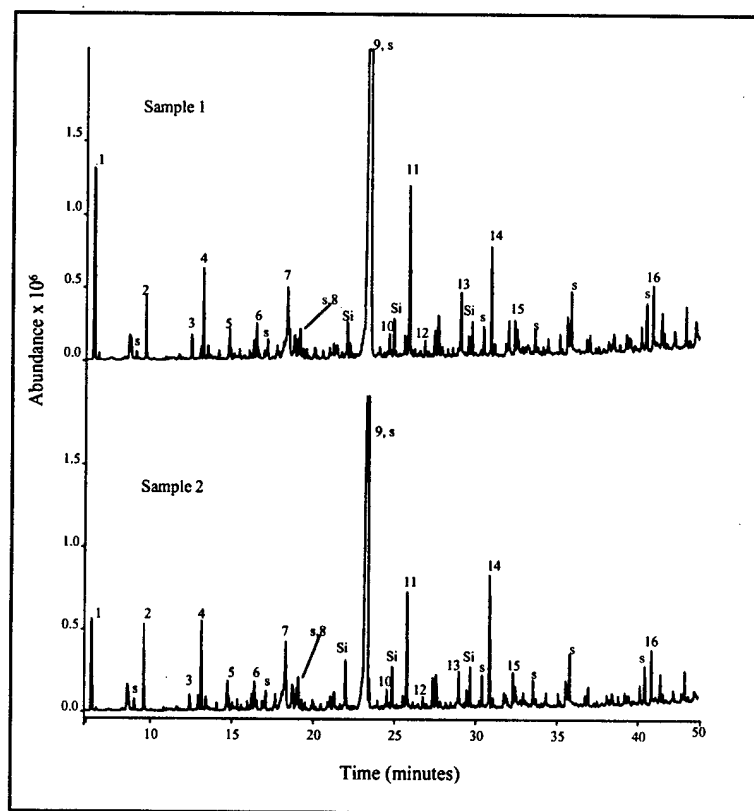

Figure 16. SVOC from NG slums incineration: adsorbate fractions.

Table 17. Identification of compounds present in the SVOC NG slums adsorbate fraction (Figure 16).

Peak	Identification	Major Ions
1	Chloroform	85 83
s	2-Fluorophenol	112 92 83 63
2	Furancarboxaldehyde	97 96 95
3	Alkylbenzene	134 119 103 91
4	Benzaldehyde derivative	155 105 77 51
5	Benzofuran and Methylfurancarboxaldehyde	118 89 63 and 109 53
6	Benzonitrile	103 76 50
s	Nitrobenzene-d5	128 98 82 70
7	Ethylbenzaldehyde and benzoic acid	133 119 105 91 and 122 105 77 51
s	Naphthalene-d8	136 108 76
8	Naphthalene	128 102
9	Triacetin	159 145 116 103 74
s	2-Fluorobiphenyl	172 152 133 98 85
10	Hydroxybenzaldehyde	121 93 65
11	Hydroxymethoxybenzaldehyde	151
12	Hexanedioic acid	231 171 149 129 111 96 79 65
13	Hydroxymethoxynitrobenzene	169 153 139 123 111 96 79 65
s	2,4,6-Tribromophenol	332 250 222 141
14	Unidentified	405 327 249 156 91
15	Hydroxymethoxynitrobenzaldehyde	197 180 149 135 122 107 93 79
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
s	p-Terphenyl-d14	244 212 160
16	Dihydronitrophenanthrylamine	240 225 209 194 165

Many of the compounds observed in the adsorbate fraction were found in the condensate fraction (Figure 17). The compounds of the condensate fraction are listed in Table 18. Again, triacetin is the dominant peak (8). The series of compounds hydroxybenzaldehyde (9), hydroxymethoxybenzaldehyde (10), hydroxy-methoxynitrobenzene (11), and hydroxymethoxynitrobenzaldehyde (14) is unexpected. Furancarboxaldehyde (2) and the benzaldehyde derivative (4) are observed at the level of the standards. Water soluble compounds are observed in the condensate fraction related to phenol (3) including dihydroxytoluene (5) and methylphenol (12).
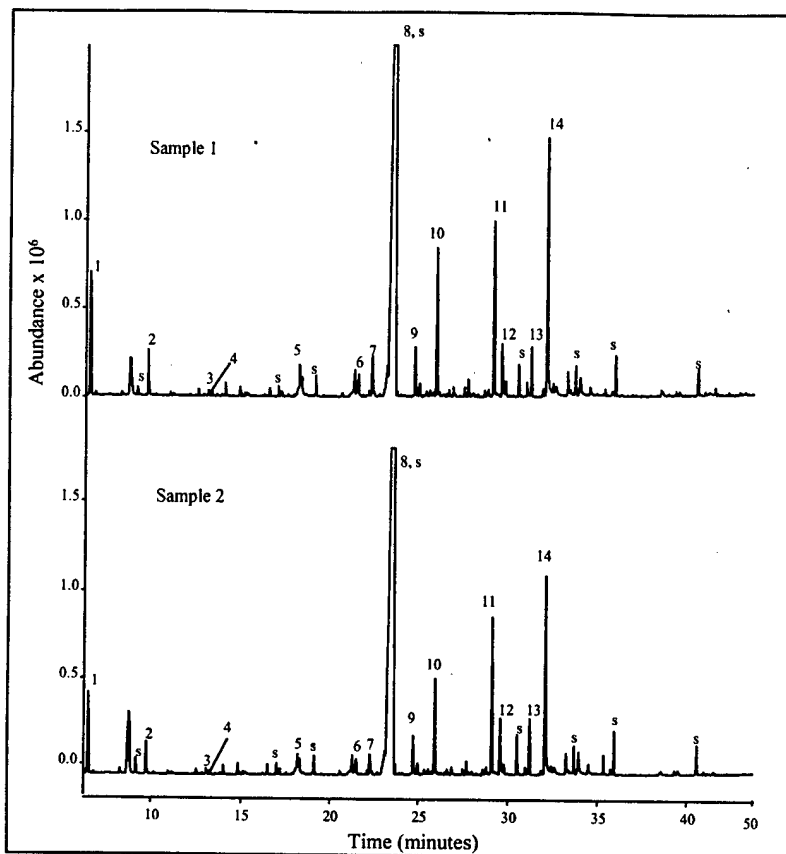
Figure 17. SVOC from NG slums incineration: condensate fractions.

Table 18. Identification of compounds present in the SVOC NG slums condensate fraction (Figure 17).

Peak	Identification	Major Ions
1	Chloroform	85 83
s	2-Fluorophenol	112 92 83 63
2	Furancarboxaldehyde	97 96 95
3	Phenol	94 66
4	Benzaldehyde derivative	155 105 77
s	Nitrobenzene-d5	128 98 82 70
5	Dihydroxytoluene and Benzoic acid	125 123 95 and 122 105 77 51
s	Naphthalene-d8	136 108 76
6	2,4-Dihydro-5-phenyl or Phenyl propenal	159 117 103 74
7	Hydroxymethylfurancarboxaldehyde	126 109 97 81 69
8	Triacetin	159 145 103 74
s	2-Fluorobiphenyl	172 152 133 98 85
9	Hydroxybenzaldehyde	121 93 65
10	Hydroxymethoxybenzaldehyde	151
11	Hydroxymethoxynitrobenzene	169 153 139 123 111
12	Methylphenol	166 151 135
s	2,4,6-Tribromophenol	332 250 222 141
13	Unidentified	169 140 112 69
14	Hydroxymethoxynitrobenzaldehyde	197 180 150 135 122
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
s	p-Terphenyl-d14	244 212 160

The filtrate fractions (Figure 18) had the fewest peaks, as expected. Table 19 lists the identifications of the labeled compounds. Triacetin (5), hydroxymeth-oxybenzaldehyde (9), hydroxymethoxyfurancarboxaldehyde (4), and furancar-boxaldehyde (3) were all observed once again. Peak 2 is probably the pentanone compound that was seen in both the NC fines and AA2 samples (see below). Peak 8 is unidentified and is the same compound noted in the adsorbate fraction (peak 14).
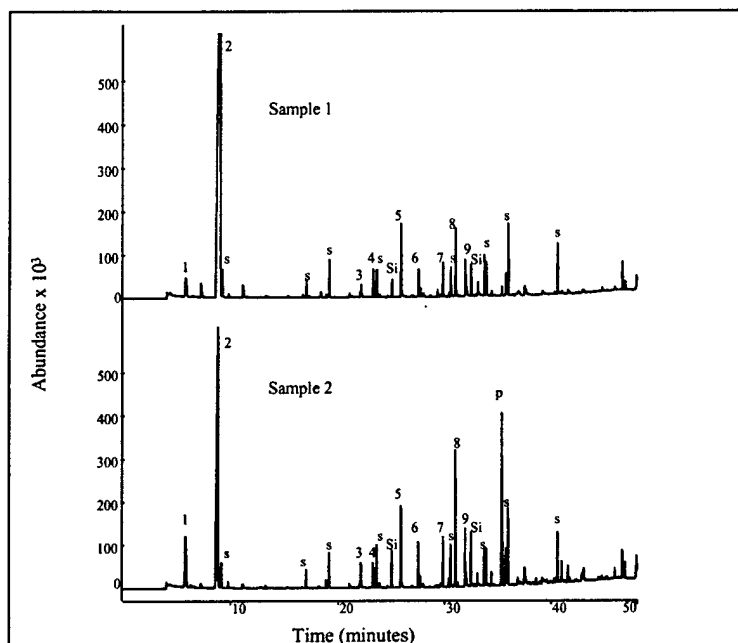

Figure 18. SVOC from NG slums incineration: filtrate fractions.

Table 19. Identification of compounds present in the SVOC NG slums filtrate fraction (Figure 18).

Peak	Identification	Major Ions
1	Toluene	91 65
2	4-Hydroxy-4-methyl-2-pentanone	116 98 83 69 59
s	2-Fluorophenol	112 92 83 63
s	Nitrobenzene-d5	128 98 82 70
s	Naphthalene-d8	136 108 76
3	Furancarboxaldehyde	96 95 67
4	Hydroxymethoxyfurancarboxaldehyde	126 109 97 81 69
s	2-Fluorobiphenyl	172 152 133 98 85
5	Triacetin	159 144 115 103 74
6	Hydroxymethoxybenzaldehyde	151
7	Hydroxymethoxybenzonitrile	149 134 106
s	2,4,6-Tribromophenol	332 250 222 141
8	Unidentified	405 327 249 156
9	Hydroxymethoxybenzaldehyde	182 167 153 139 111 93 65
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
s	p-Terphenyl-d14	244 212 160

AA2 Samples — SVOC

Two semivolatile samples were collected during the incineration of AA2. The chromatograms of the two samples are shown in Figures 19 - 21, which represent the adsorbate, condensate, and filtrate fractions, respectively. The samples show good reproducibility for each fraction. All seven laboratory standards and the surrogate standard are observed for all three fractions.

Semivolatile analysis from the incineration of AA2 is far richer in information than the VOC analysis. More compounds are present but at lower abundances than in the AA2 VOC adsorbate fraction (Figure 9). Table 20 lists the identified SVOC in the adsorbate fraction. The ion trap's lower mass scan range of 50 amu again hindered peak identifications. Better identification was obtained by performing complementary analyses with a quadrupole GC/MS set to detect masses down to 10 amu. The largest peak (16) is di-n-propyladipate, a minor component of AA2. Many of the prominent peaks following peak 16 are siloxanes that are likely from column or septum degradation. A few interesting compounds that elute among the siloxanes were phenazine (17), carbazole (18), bis(p-tert-butylphenyl)ether (19), and 2-nitro-N-(4-nitrophenyl)benzamine (21). Peak 20 is NDPA, also an additive of AA2, and therefore a POHC. Another observed POHC is triacetin (15), which was also detected in the NC fines and NG slums samples.
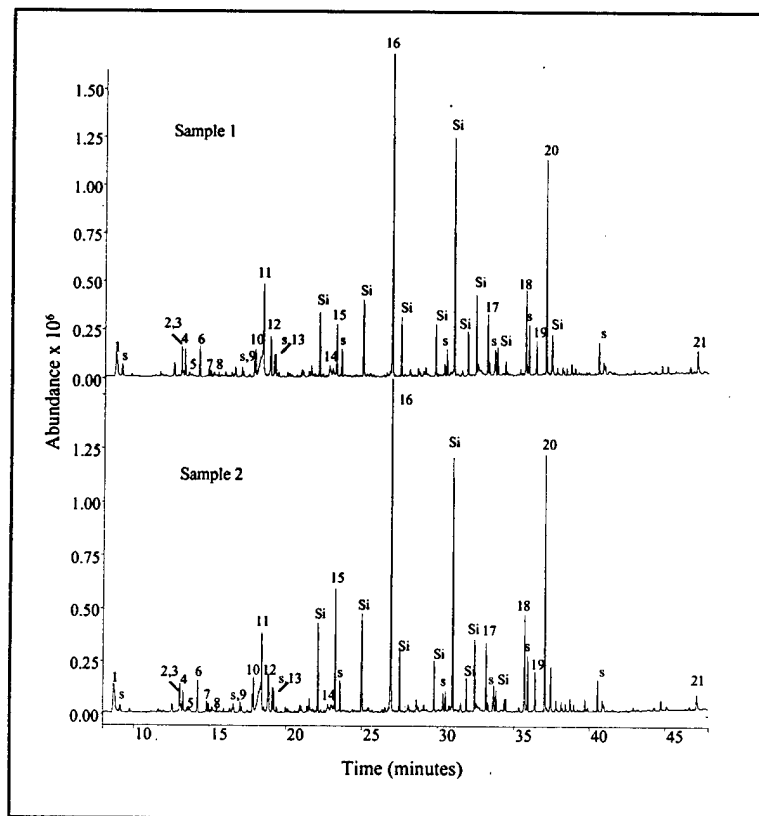

Figure 19. SVOC from AA2 incineration: adsorbate fractions.

Table 20. Identification of compounds present in the SVOC AA2 adsorbate fraction (Figure 19).

Peak	Identification	Major Ions
1	4-Hydroxy-4-methyl-2-pentanone	116 98 83 59
s	2-Fluorophenol	112 92 83 63
2	Phenol	94 66
3	p-Benzoquinone	108 97 83 69 54
4	Benzaldehyde	105 77 51
5	Benzofuran	118 109 89 63
6	Benzonitrile	103 76 50
7	Benzoxazole or 2-Hydroxybenzonitrile	119 91 74 63
8	Hydroxybenzaldehyde	121 104 93 65
s	Nitrobenzene-d5	128 98 82 70 54
9	Nitrobenzene	123 105 93 77 51
10	Nitrophenol	139 122 109 92 81 63 53
11	Benzoic acid	122 105 77 51
12	Ethylbenzaldehyde	133 119 105 91 77 65 51
s	Naphthalene-d8	136 108
13	Naphthalene	128 102
14	Ethylbenzoic acid	150 135 105 91 77
15	Triacetin	159 145 116 103 74
s	2-Fluorobiphenyl	172 146
16	Di-n-propyladipate	230 171 142 129 111
s	2,4,6-Tribromophenol	332 250 222 141
17	Phenazine	180
s	Phenanthrene-d10	188 160
18	Carbazole	167
s	PCB	292 255 220 184 150 110
19	Bis(p-tert-butylphenyl)ether	282 267
20	NDPA	214 197 180 167
s	p-Terphenyl-d14	244
21	2-Nitro-N-(4-nitrophenyl)benzamine	259

Table 21 lists the compounds found in the condensate. A considerable number of the SVOC observed in the adsorbate fraction are also found in the condensate fraction (Figure 20) indicating breakthrough from the XAD trap. The common species are peaks 5-8 and peaks 12-16. Isoquinoline (11) and phenylpropenal (10) were also detected in the adsorbate fraction at a very low level, leaving peaks 3, 4, and 9 as newly observed species.
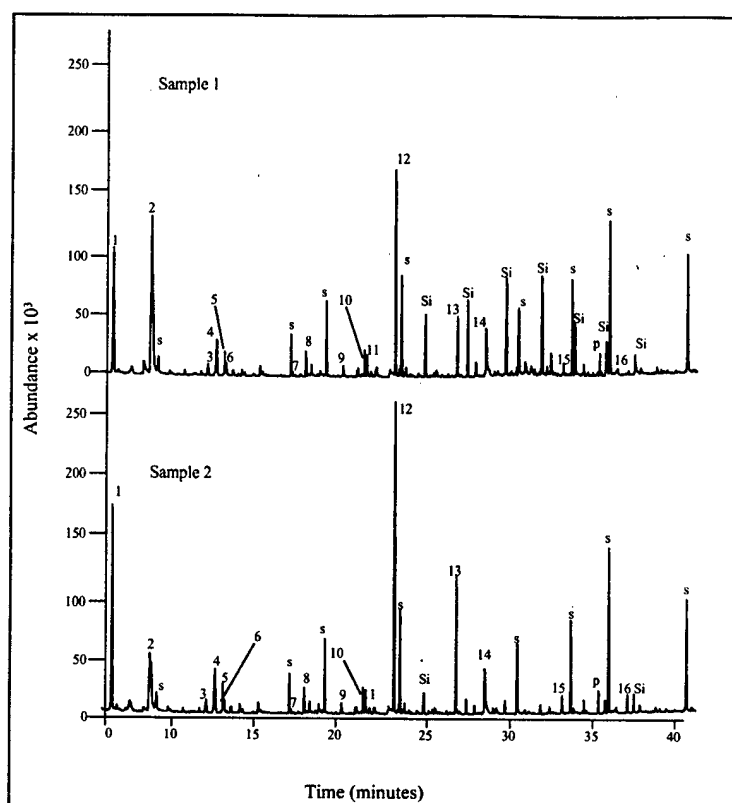
Figure 20. SVOC from AA2 incineration: condensate fractions.

Table 21. Identification of compounds present in the SVOC AA2 condensate fraction (Figure 20).

Peak	Identification	Major Ions
1	Chloroform	85 83
2	4-Hydroxy-4-methyl-2-pentanone	116 98 83 59
s	2-Fluorophenol	112 92 83 63
3	$C_7H_{16}O$	116 87 69 59
4	C_9H_{16}	104 77 69 55
5	Phenol	94 66
6	p-Benzoquinone	108 97 83 69 54
s	Nitrobenzene-d5	128 98 82 70
7	Nitrobenzene	123 105 93 77 51
8	Nitrophenol	139 122 109 92 81 63 53
s	Naphthalene-d8	136 108 76
9	Pyridinecarbonitrile	104 77
10	3-Phenyl-2-propenal	131 122 103 77 51
11	Isoquinoline	129 102
12	Triacetin	159 145 116 103 74
s	2-Fluorobiphenyl	172 152 133 98 85
13	Di-n-propyladipate	230 171 142 129 111
14	Nitrophenol	139 122 109 92 81
s	2,4,6-Tribromophenol	332 250 222 141
15	Phenazine	180
s	Phenanthrene-d10	188 160 132 94 80
s	PCB	292 255 220 184 150 110
16	NDPA	214 197 180 167
s	p-Terphenyl-d14	244 212 160

Analysis of the extract of the particulate filter (Figure 21) revealed the least number of SVOC of any fraction, which is reasonable since the high temperature of the gases at the sampling point should prevent the SVOC from condensing onto the particulates. The majority of the peaks in the chromatogram were identified as phthalates and siloxanes and were omitted from the list of compounds in Table 22. The sulfamide compounds (7 and 8) are unexpected and are detected in only one of the two filtrate samples. The library matching for these compounds was good, however, and the only explanation for their presence is reactions of by-products with sulfur compounds that are added to natural gas for its detection. Squalene (9) was also observed in the background. The toluene peak (1) is again large. Peaks 2, 3, 4, and 5 are simple polar compounds. All are relatively small, except for the pentanone compound, which is also pronounced in the condensate.
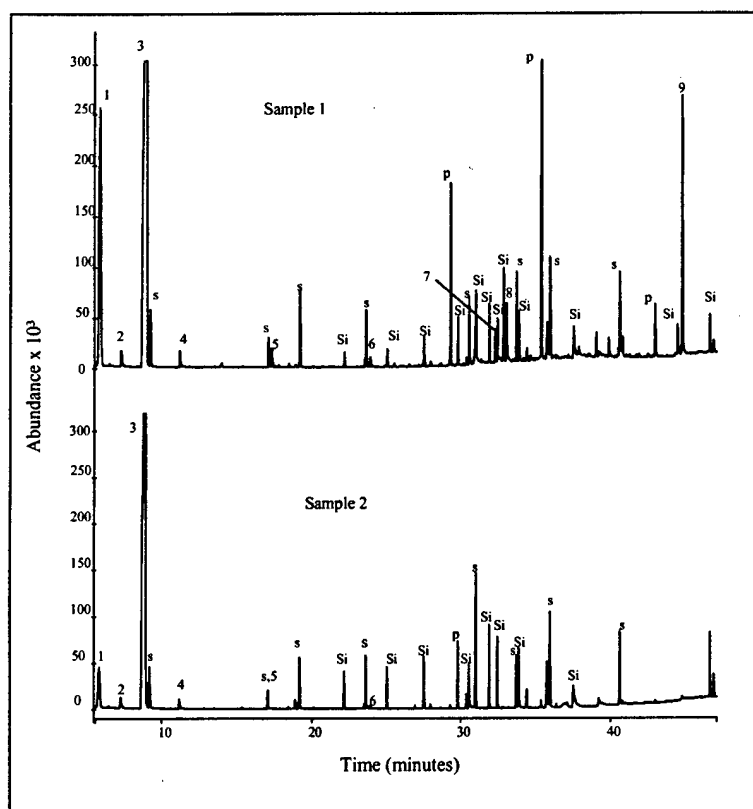

Figure 21. SVOC from AA2 incineration: filtrate fractions.

Table 22. Identification of compounds present in the SVOC AA2 filtrate fraction (Figure 21).

Peak	Identification	Major Ions
1	Toluene	92 91 65
2	$C_6H_{10}O$ or C_7H_{14}	98 83 55
3	4-Hydroxy-4-methyl-2-pentanone	116 98 83 59
s	2-Fluorophenol	112 92 83 63
4	$C_8H_{16}O_3$	133 116 98 87 69 58
s	Nitrobenzene-d5	128 98 82 70 54
5	$C_{10}H_{16}O$	152 108 95 81 67 55
s	Naphthalene-d8	136 108 76 66 54
s	2-Fluorobiphenyl	172 152 133 98 85
6	Hexanedioic acid, bis(1-methylethyl)ester	171 141 129 111 100 83 73 55
s	2,4,6-Tribromophenol	332 250 222 141
7	2-Methylbenzenesulfamide	171 154 137 106 90 77 65 51
8	4-Methylbenzenesulfamide	171 155 107 91 65
s	Phenanthrene-d10	188 160
s	PCB	292 255 220 184 150 110
s	p-Terphenyl-d14	244 212 160
9	Squalene	341 231 189 135 121 107 95 81

For completeness, Figures 22 – 24 show the chromatograms for the three AA2 SVOC fractions analyzed by the quadrupole GC/MS. The features are quite similar to the results shown above from the ion trap. Of particular interest is the peak that eluted at 15 min in the adsorbate and condensate fractions. This peak has the mass fragments 76, 46, and 30 amu, indicative of NG. In addition, analysis of an NG standard has an identical retention time of 15 min. These data show that NG was also present in the incinerator emissions as a POHC.
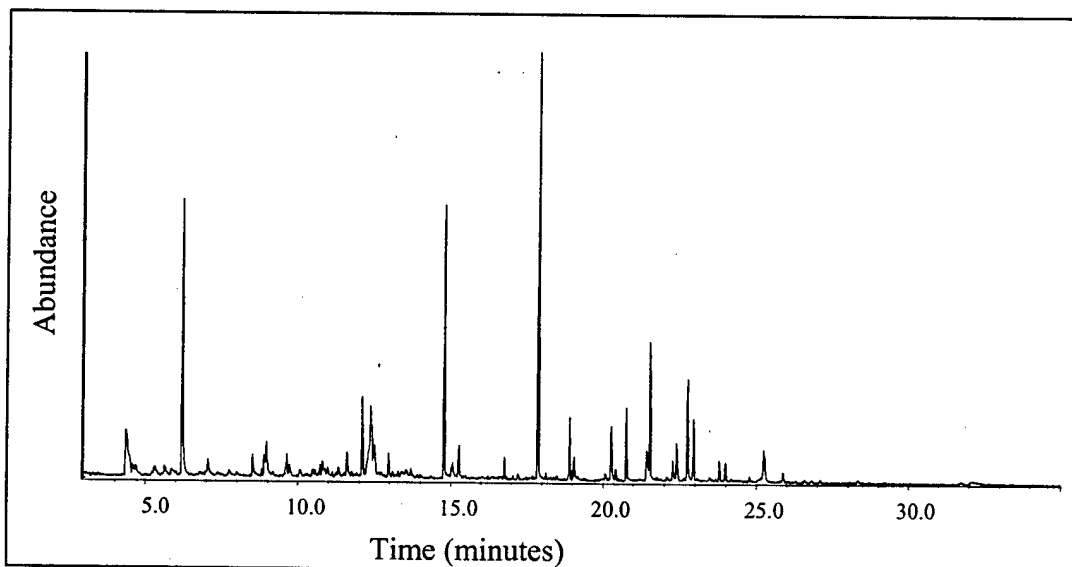

Figure 22. SVOC from AA2 incineration analyzed by quadrupole GC/MS: adsorbate fraction (Filename: RAAP22.D).
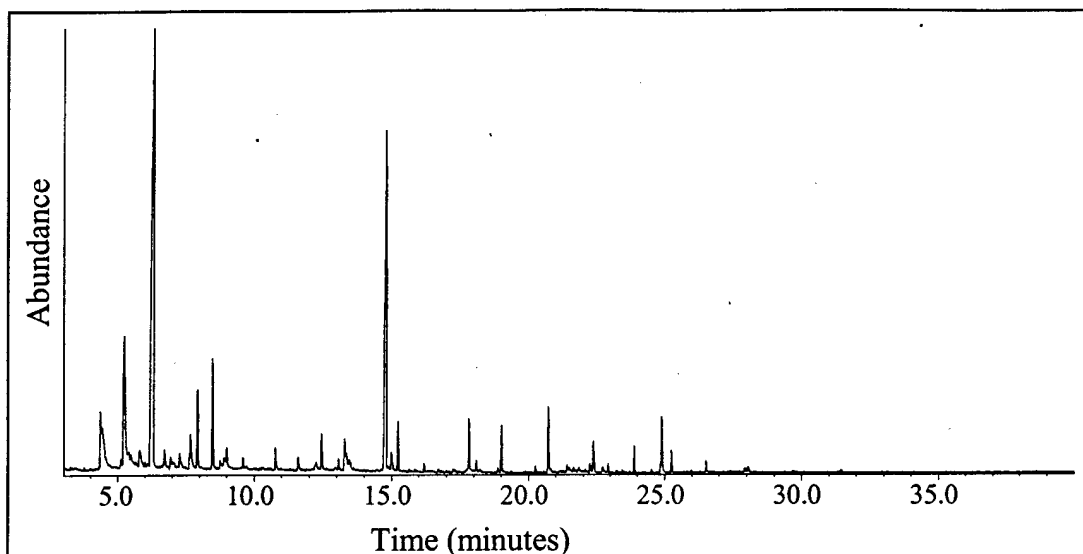
Figure 23. SVOC from AA2 incineration analyzed by quadrupole GC/MS: condensate fraction (Filename: RAD22CCR.D).
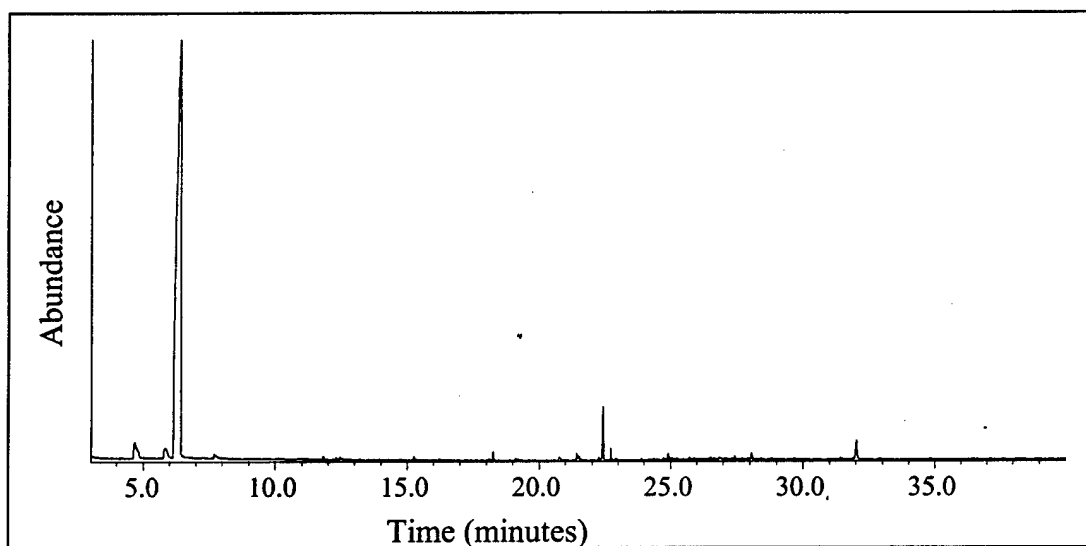

Figure 24. SVOC from AA2 incineration analyzed by quadrupole GC/MS: filtrate fraction (Filename: RAD22FLT.D).

HCN Analysis

Incineration Background Samples

Table 23 shows the HCN analysis results for the background sample. The level of HCN generated during combustion of natural gas alone is low, measuring 0.9 ppm for the background samples.

Table 23. HCN of incinerator background.

Sample Fraction	HCN (ppm)	pH
Condensate	0.9	11
Filtrate	0.9	14

NC Fines Samples

Review of Table 24 suggests that some HCN may have been produced during the incineration of NC fines. The slight elevation above the background level, however, is within experimental error. The lack of HCN may be a result of exceeding the maximum sample holding time of 5 days (NIOSH 1994). This may be reflected in the pH values, especially for Filtrate - 1.

Table 24. HCN from NC fines incineration.

Sample Fraction	HCN (ppm)	pH
Condensate - 1	0.9	12
Condensate - 2	1.3	13
Condensate - 3	1.5	13
Filtrate - 1	0.9	7
Filtrate - 2	0.9	12
Filtrate - 3	0.9	12

NG Slums Samples

The results for NG slums are shown in Table 25. No appreciable amount of HCN is detected. Again, analysis occurred after the maximum holding time.

Table 25. HCN from NG slums incineration.

Sample Fraction	HCN (ppm)	pH
Condensate - 1	0.9	12
Condensate - 2	0.9	11
Condensate - 3	0.9	12
Filtrate - 1	0.9	14
Filtrate - 2	0.9	14
Filtrate - 3	0.9	13

AA2 Samples

Table 26 shows the result of analysis for HCN. None of the samples contained an amount of HCN above the background level.

Table 26. HCN from AA2 incineration.

Sample Fraction	HCN (ppm)	pH
Condensate - 1	0.9	12
Condensate - 2	0.9	11
Condensate - 3	0.9	12
Filtrate - 1	0.9	14
Filtrate - 2	0.9	14
Filtrate - 3	0.9	13

CEM Analysis

The five gases measured by CEM include THC, NO_x, O_2, CO, and CO_2. These gases are measured continuously over an entire incineration run. The data obtained for the AA2 run are shown in Figure 25. The x-axis measures time intervals and the y-axis measures the concentration of the light gas. Time interval 1 to time interval 60 corresponds to approximately a 10-hr real-time span. The gas concentration value is the average over that time interval. AA2 was being fed into the incinerator constantly over the course of these time intervals. The feed was stopped, however, to allow personnel to approach the sampling equipment. The stopped times correlate to time intervals 16, 28, 32, 36, and 47 in Figure 25.

The NO_x data in Figure 25(a) show a slightly sloping baseline that eventually levels off near time interval 25. During feed times, the NO_x level was high (650 ppm) and during the stop times, the NO_x level dropped to 50 ppm. This indicates that NO_x is produced during incineration of AA2. CO (Figure 25(b)) showed similar behavior. It leveled off to a plateau of 200 ppm at time interval 25. CO dropped to 10 ppm during the stop times. Thus, CO is also produced during AA2 incineration.

CO_2 has a more consistent baseline over the entire time period with a measured CO_2 concentration of 5.5 percent during incineration (Figure 25(c)). When AA2 is not incinerated, the CO_2 level is about 4 percent. This indicates CO_2 production during AA2 incineration.

O_2 shows a different behavior (Figure 25(d)). When AA2 is incinerated, the O_2 level is constant near 11 percent. The O_2 output increases, however, when AA2 is not incinerated. This result is expected because O_2 is consumed during incineration.
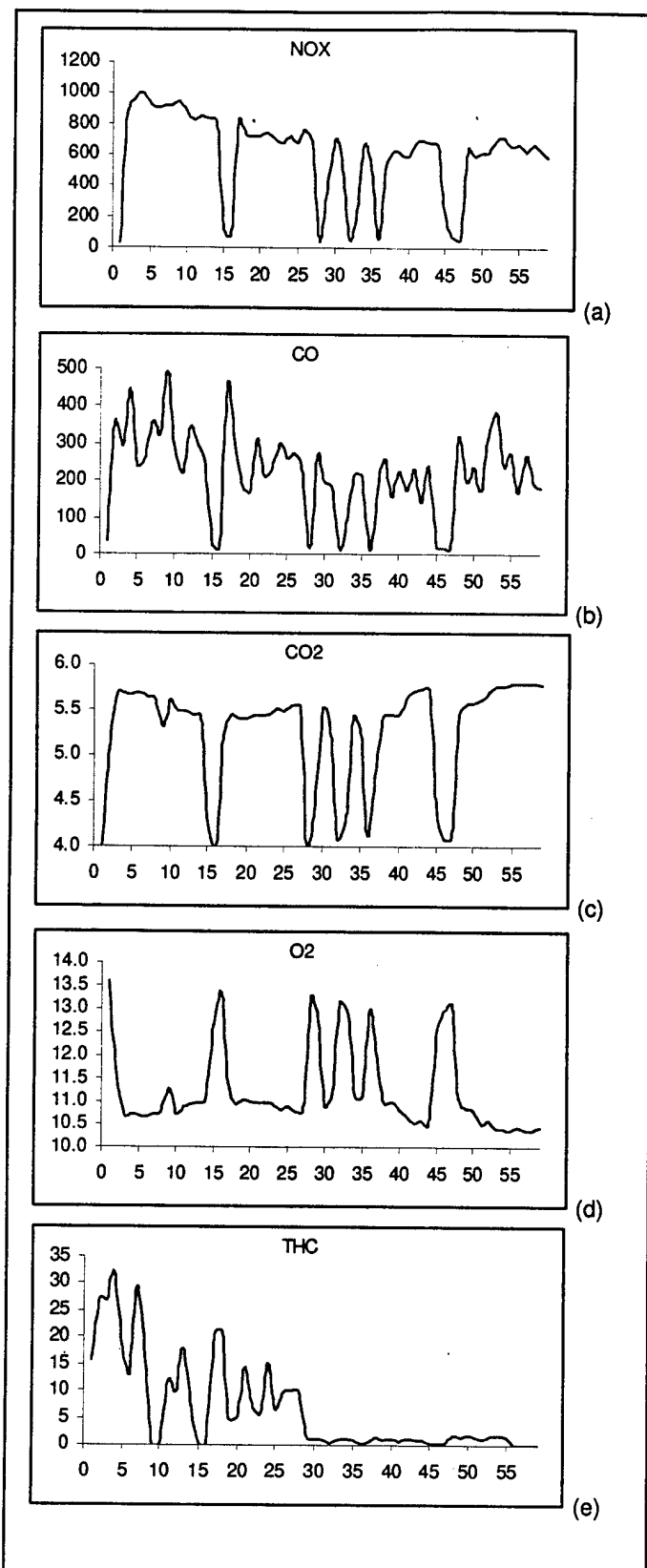
Figure 25. CEM sampling data from 1 day of burns
averaged every 10 minutes.

The THC data shown in Figure 25(e) indicates instrumental problems. THCs are expected to increase in the presence of AA2 since POHC and PIC will be produced. During the down times, THC should decrease to a level commensurate with the burning of natural gas. Figure 25 shows that the THC level dropped to zero over the course of the day and did not recover.

CEM data for the NC fines and NG slums mimics the AA2 data and is not shown. This instrumentation merely shows that NO_x, CO, and CO_2 are incineration emission products, while O_2 is consumed during the burn.

4 Conclusions

By collecting incineration by-products between the rotary kiln and the after-burner, compounds due solely to incineration can be isolated and analyzed. This type of information can help optimize operational parameters for the remaining treatment components to ensure complete degradation of the effluent gases.

All three waste feeds produced similar sets of VOC by-products, each having few unique features. NG slums and AA2 generated the most VOC PIC while NC fines had far fewer. Furan type compounds were detected in all VOC samples.

The SVOC adsorbate fraction provided the best signature for each waste feed. The NC fines by-products are dominated by contributions from the anti-foaming agent with numerous regular hydrocarbon peaks. Similarly, by-products from NG slums are primarily due to the cellulosic and deactivator additives since the energetic compound NG is not expected to produce many SVOC. The AA2 sample contained many POHC from the trace additives in its formulation. Condensate and filtrate fractions typically had no new additional by-products.

Since AA2 is primarily composed of NC and NG (>90%), it is conceivable that the incinerator by-products might have been a summation of NC and NG by-products. The above data indicate that this is not the case. Instead, this research illustrates that, for high energy components, the SVOC by-products are dominated by the minor additives in the waste feed and, furthermore, there may be interactions between the by-products that cannot be ignored.

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Acronyms and Abbreviations

CEM	continuous emission monitors
CO	carbon monoxide
CO_2	carbon dioxide
DNT	dinitrotoluene
EM	energetic material
EPA	U.S. Environmental Protection Agency
EW	energetic wastes
GC/MS	gas chromatography/mass spectrometry
HCN	hydrogen cyanide
NC	nitrocellulose
NG	nitroglycerin
NIOSH	National Institute for Occupational Safety and Health
NO_x	nitrogen oxides
NDPA	2-nitrodiphenylamine
OB/OD	open burning/open detonation
O_2	oxygen
PIC	products of incomplete combustion
POHC	principal organic hazardous constituents
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
SVOC	semivolatile organic compound
THC	total hydrocarbons
VOC	volatile organic compound
VOST	Volatile Organic Sampling Train

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14. ABSTRACT
Incineration is one technology used for thermal treatment of energetic materials (EM) and associated energetic wastes (EW). Knowledge of the by-products from incineration is invaluable for the proper design of emission control systems and selection of operating parameters to ensure maximum destruction efficiency. This project focuses on uncovering the by-products resulting from the incineration of EM and EW. The sampling and analysis of by-products from a hazardous waste incinerator were performed at an Army installation during the burning of several Army waste streams.

The three EW burned at this rotary kiln incinerator are nitrocellulose (NC) fines, nitroglycerin (NG) slums, and AA2, a solventless double base propellant. Combustion by-products were collected from a sampling port located between the rotary kiln and incinerator afterburner, upstream of all pollution control devices. Several different sample collection trains were used for characterization of the by-products including volatile and semi-volatile organic compounds, hydrogen cyanide, carbon monoxide, nitrogen oxides, and total hydrocarbons.

The collection plan, the instrumental set-up, and the analytical results are presented for the incineration of all three EW listed above. The challenges and problems encountered during sample collection at the incinerator kiln port are discussed as well as solutions used to overcome these problems.

15. SUBJECT TERMS
hazardous waste management, energetic materials (EM), energetic waste (EW), munitions waste disposal, incineration, emissions

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